INVESTIGATION OF THE MONOLAYERS OF POLYOXYETHYLENE-OCTADECANOL (PEO) AT AIR-AQUEOUS SOLUTION INTERFACE

INAUGURAL-DISSERTATION
zur
Erlangung der Doktorwürde

eingereicht beim
Fachbereich Physikalische Chemie
der Philipps-Universität Marburg/Lahn

vorgelegt von

S. SAKHAWAT SHAH
aus Haripur/Pakistan

Marburg/Lahn 1977

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Berichterstattet: Prof. Dr. W. Luck
Mitberichterstatter: Prof. Dr. H. Lange

To my father,

who wished me to be a doctor.

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INTRODUCTION

The structure of water is sensitive to the temperature and the added salts [1]. Since the early studies on water by Röntgen in 1892 a number of methods have been used for water research, but nowadays the spectroscopic methods are preferred. Some surface tension experiments have been used to relate the properties of bulk water to the interfacial water by some authors [2,3]. However, a simple and direct way of influencing the water structure at the air-water interface is to spread a monolayer of an insoluble surfactant. It is now of interest to know, whether and how the changed structure of water, either by temperature or by salt addition, affects the monolayer at the interface?

Some recent works on the specific effects of salts on monolayers and the water structure have been directed at the ionized monolayers [4,5]. Since more subtle effects on the interfacial water structure are diluted by the large electrostatic interactions, it seems necessary to use unionized monolayers, such as long-chain alcohols and long-chain alkoxy alcohols, to emphasize the specific salt effects on the water structure at interfaces. Until recently very little attention was paid to the study of the ionic effects on the unionized monolayers. Therefore it is considered to be necessary to study substances as spread monolayers, which are non-ionic and susceptible to hydration through the formation of hydrogen bonds. Since the hydrogen bond formation is sensitive to temperature and added electrolytes, the water structure in bulk as well as the interface changes by both factors. Since the polyethylene oxides are well suited for the hydrogen bond formation with water molecules and are non-ionic in nature, their derivatives "polyoxyethylene-octadecanol (PEO)" are chosen

Fig. 1. The structural formulas of polyoxyethylene-octadecanol (PEO); octadecanol (OD), monooxyethylene-octadecanol (MEO), dioxyethylene-octadecanol (DEO), trioxyethylene-octadecanol (TEO), quadrooxyethylene-octadecanol (QEO).

as spreading substances. It is worth mentioning that along many other industrial applications PEO have recently won the attention of many workers for the use of minimizing the loss of water by evaporation in reservoirs (6).

To study the intermolecular interaction between the hydrophilic groups of PEO film molecules and water, three variables have been chosen for the measurements of PEO monolayers,

a) the hydrophilicity of film molecules

b) temperature variation

c) changes in structure of water by salt addition.

By the addition of ethyleneoxide (EO) units with octadecanol, the latter becomes more hydrophilic. Hence the polyoxyethylene-octade-

canol (n= 0,1,..4 and n= 9) have been measured as F-A curves and ΔV-A curves at the air-water interface. The formulae of PEO are shown in fig. (1). For the temperature measurements of PEO (n =1,2,3) the temperature was varied between 12 ^{o}C and 35 ^{o}C. A number of salt solutions (1m) like Na_2SO_4, NaCl, $NaNO_3$ and $NaClO_4$ have been used as substrates to study the influence of various anions on the PEO monolayers. Sodium perchlorate solutions (0.1m to 4m) have been used as substrates to study the concentration effects. The surface potential of some PEO members are also measured at various electrolyte solutions of 0.1m concentration. To differentiate between the effects of pH and the salts, some measurements of PEO monolayers on sodium (mono-, di-, and tribasic) phosphate solutions are further performed.

In the present work discussion has been made in terms of the intermolecular interaction between the hydrophilic groups of PEO molecules and water molecules, hydration, energy of dehydration, and configuration of the film molecules as fuction of HHB, temperature and nature of the substrate. The temperature effects are further correlated with the HHB effects. The salt effects are compared with the Hoffmeister series of anions [7], and the comparative effects of various anions upon PEO monolayers are considered in 'structure-breaking' and 'structure-making' terms and compared with the spectroscopic determined 'structure temperatures' of the studied salts. With comparison to the literature works the pH and salt effects have been considered by studying the effects of sodium mono-, di-, and tribasic phosphates on PEO monolayers. Moreover, the contribution of hydrophilic groups and the subphase molecules to the surface potentials and surface dipole moments of PEO, as well as the variation of both quantities by the presence of salts in the subphase are also considered.

2. Literature Survey

2.1 Structure of water

Of all known liquids water is probably the most studied and the least understood, although many of its physical properties are accepted as international standards, e.g., its triple point, density, mass and viscosity etc. The behaviour of water in any of its phases depends ultimately upon the structure and the properties of the isolated water molecules. The modern history of the structure of water was started by Röntgen [8], who explained several of its apparently anamolous properties qualitatively. The concept of hydrogen-bonding was first recognized by Moore and Winemill [9] and was extended by Latimar and Rodebush [10]. Stewart[11] described liquids as a mixture of large aggrigates and monomers. Nemethy and Scheraga [12] presented the quantitative model of cluster sizes of water molecules, however, using five adjustible constants. Recent interest in the structure of water has developed so intensely that there is a large number of standard books and monographs on water [13,14,15].

The availability of the free orbitals (with lone electron pairs) on the oxygen atom causes the electrostatic bonding onto two other hydrogen atoms. This is what happens in a crystal of ice and liquid water at low temperatures.

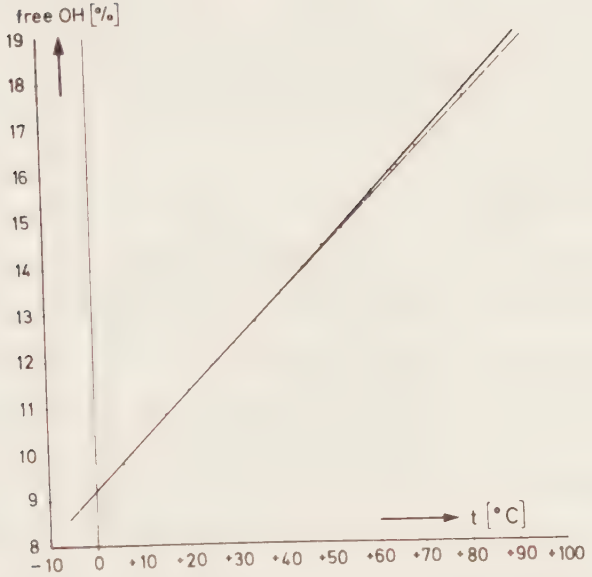


Fig. 2. The increasing percentage of non H-bonded OH groups in liquid water as function of temperature [14]

Luck [1] pointed out that the water consists of a network of hydrogen-bonded molecules, and showed the method to calculate the non-hydrogen-bonded -OH groups quantitatively without using any adjustable constant. Using the IR overtone method Luck [14] showed the sensitivity of the hydrogen-bonding phenomenon as a function of temperature (see fig.2). The content of non-H-bonded OH groups is about 11 % at room temperature, but increases with the increasing temperature, which means the breaking of hydrogen-bonded water structure.

On the basis of non-polar liquids Luck [1] presented a " hole-model theory" for the liquids, which includes a thermal vibration volume and the dependent hole defects in liquids. Along many other properties like density, specific heat, heat

vaporization etc., the Raoults law (i.e., the decrease of vapour pressure of a solution is proportional to the solute concentration) could be explained with this simple 'hole-model theory'.

2.2 Aqueous Solutions

The properties of water are largely influenced by the presence of ions in it. The ionic effects can be understood by the assumption that the electric field of the ion strengthens the orientation of the water dipoles by H-bonds, but the larger anions, usually structure-breakers, disturb the long range orientation of the H-bond system [15]. The orientation of the water dipoles around the ion leads to the hydration or solvation of the ion. Due to the operation of these ion-dipole forces three spheres or regions of water molecules around the ion have been classified by Bockris [16]; primary hydration region, secondary hydration region and the bulk water.

The structure changing behaviour of ions depends upon the nature and size of the ions; the anion's effects are higher than the cation's effects [17]. Hoffmeister [7] found the effects of some inorganic ions upon the flocculation of albumin in the following order:

sulphate > chloride > nitrate > chlorate.

Bruins [18] calculated the "lyotropic numbers" of various anions and cations from the results on agar-agar sols and gelatine, and gold-sol respectively. The lyotropic numbers of various anions and cations are found in the following orders:

$$CNS^- > I^- > ClO_4^- > NO_3^- > Br^-$$

and $$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$$

The meaning of the lyotropic numbers has been related to the heats of hydration for the anions, and to the ionizing potentials of the cations [18,19,20]. Since the heat of hydration of the ions depends upon the electric field which surrounds them, the lyotropic effects are beyond doubt caused by the different electric field strengths of the ions [21]. Moreover, the heats of hydration are in direct relation with the radii of the ions [20,22]. Recently some workers confirmed the 'Hoffmeister series' of ions by measuring the critical micelle concentration and adsorption of the non-ionic surfactants [23,24]. Luck [15] identifies the cause of the lyotropic ion series with the effects on the water structure.

Bernal and Fowler [25] defined the 'structural temperature' ($T_{str.}$) as the temperature of an aqueous solution to be equal to that of pure water when the content of the hydrogen

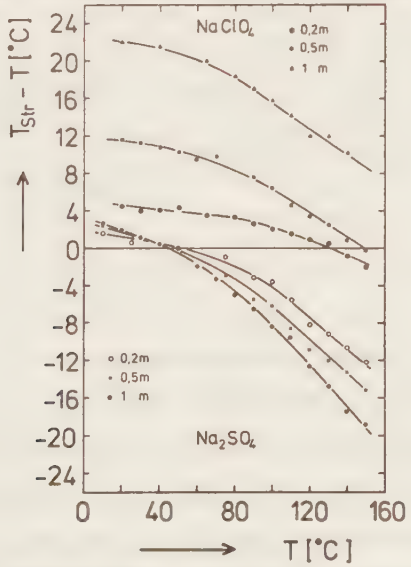


Fig. 3. $T_{str.}$ - T for $NaClO_4$ and Na_2SO_4 solutions of 0.2, 0.5 and 1 mole/L against T (°C)[26]

bonds of aquous solution is equivalent to that of pure water. Luck [26] gave a spectroscopic method for determining $T_{str.}$ quantitatively and used $T_{str.}$ as a measure to classify the ions into 'structure-breaker' and 'structure-maker' groups. In fig. (3) he plotted $T_{str.}$-T for $NaClO_4$ and Na_2SO_4 at different molar concentrations against T (^oC). For structure-breakers the value of $T_{str.}$-T is more than zero and for structure-makers less than zero. Hence $NaClO_4$ becomes much more structure-breaker with increasing concentration, whereas Na_2SO_4 shows the reverse effects. However, at lower temperature Na_2SO_4 acted also as a structure-breaker.

The structure-breaking ion increases the concentration of the non-H-bonded OH groups, hence such ions show the " salting-in " effects upon the organic molecules [26]. Anions with larger radii are usually structure-breakers. Structure-makers, on the other hand, decrease the concentration of the non-H-bonded OH groups and have a " salting-out " effect upon the organic phases. Luck [15] elaborated the salting-in and salting-out behaviour by measuring the turbidity point (T_k) and water content of $H_{17}C_8-C_6H_4-(OCH_2CH_2)_9OH$ (PIOP-9) in presence of various salts in water. The influence of the Hoffmeister ion series as measure of water structure on the water content of organic phases in aquous two-phase systems (H_2O / PIOP-9) is found in following order:

$$NaSCN > NaClO_4 > NaNO_3 > NaCl > NaBr > Na_2CO_3 > Na_2SO_4$$

The addition of salts has similar effects upon the spectrum of water as observed by changing the temperature [13]. The concentration effects of $NaClO_4$ upon shifting of the bond towards higher wave numbers are shown in fig. (4) [27].

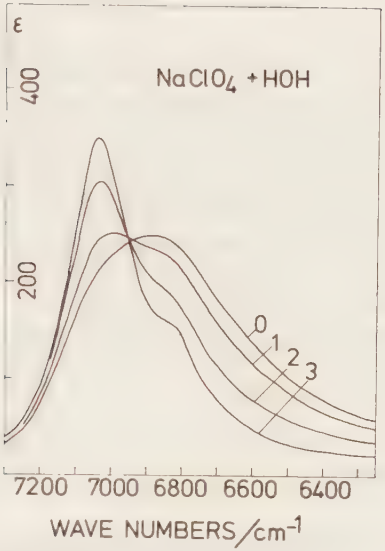


Fig. 4. Infrared spectra of $NaClO_4$ solution, (0) pure water; (1) 200g/L; (2) 400g/L; (3) 800g/L.[27].

The shifting of the water bond from 6900 to 7050 wave numbers in presence of $NaClO_4$ is due to the higher content of free OH groups than in water, and larger intensities of the bonds at 7050 wave numbers with increasing concentration of salt is due to the higher contents of free OH groups. Some other workers reported similar results for $NaClO_4$ by IR methods[28,29] and by Raman method [30].

2.3. Interfaces (air-water)

The surfaces present a good example of dissymmetry. On one side the forces are of the same order as in the interior of the liquid, whereas on the other side is vapour, in which the molecules are so far apart as to produce only a negligible field between them. It is a matter of common observation that water drops adopt a spherical shape, suggesting that the liquids may be surrounded by an elastic skin, the tension of which causes the surface to contract to the smallest possible area.

Young [31] was the first to attempt an explanation of this 'surface tension' in terms of attractive and repulsive forces between the molecules constituting the liquid. On one side of air-water interface the attraction between the neighbouring molecules of water is fulfilled most completely in the interior of the phase, while those molecules at the interface are attracted less completely than they would have been in the bulk of water.

2.3.1. Surface tension

Surface tension (γ) is usually taken as a direct measure of intermolecular interaction. In most text books the surface tension is defined as " the force, due to unbalanced molecular attraction, which tends to pull molecules into the interior of a liquid phase, and hence to minimize the surface area ". Surface tension, however, would be considered as 'energy' instead of force, since γ is a measure of the work required to increase the surface by unit area, at constant temperature, pressure and composition. It can be manifested mathmatically by the following equation,

$$dG = -SdT - PdV + \gamma dA + \mu dn \quad \ldots\ldots\ldots\ldots \quad (1)$$

where G is the Helmholtz free energy of system, S is entropy, T the absolute temperature, P, V, μ, n, and A reflex pressure, volume, chemical potential, number of moles and surface area respectively. At constant temperature and volume for a given number of moles of the system the above equation can be reduced to

$$\gamma = \left(\frac{\partial G}{\partial A}\right)_{T,V,n} \quad \ldots\ldots\ldots\ldots \quad (2)$$

then γ has the dimensions of erg/cm^2. Luck [32] emphasized the use of molar surface tension γ_M instead of γ, which is the measure of the work required to increase the surface by one mole. γ_M can be calculated by the following equation,

$$\gamma_M = \gamma N_L^{1/3} V^{2/3} \quad \ldots\ldots\ldots\ldots (3)$$

where V is the molar volume and N_L is the Loschmidt's number; $N_L^{1/3} V^{2/3}$ is the surface which is produced by N_L molecules on the surface of a liquid. The higher value of γ for water is due to the large number of H_2O molecules in 1cm^2 area [32].

2.3.2 Effect of temperature on surface tension

Surface tension is a measure of attraction between the molecules. With increasing temperature the surface tension decreases, since the molecular attraction is partially overcome with increasing temperature. An old and well-known relationship, attributed to Eötvös [33], is

$$\gamma V^{2/3} = k(T_c - T) \quad \ldots\ldots (4)$$

where V is the molar volume, T_c is the critical temperature and k is constant. From equation (4) one does expect the surface tension to go to zero at the critical temperature. This is what actually happens with chloroform and many other substances [34]. The decrease in surface tension of water with increasing temperature and vice versa has been measured by the author, the values are given in table (II.c).

2.3.3 Effects of salts on the surface tension

The addition of inorganic electrolytes to water invariably results in an increase in surface tension, whereas the organic compounds and the surface active agents lower the

surface tension [35]. Raltson and Healy [36] found the increase in surface tension of 4m salt solution containing Cl^- as common anion at 21 °C in the following order:

$Mg^{2+} > Ca^{2+} > Li^+ > Na^+ > K^+ > NH_4^+ > Rb^+ > Cs^+$.

Furthermore, with increasing concentration of KCl the surface tension was elavated [36]. They attributed these salt effects to the hydration shell of the ions concerned, and concluded that the structure-breaker like Cs^+ can more easily be accomodated in the interface than Li^+, a structure-maker. However, this approach of ions accomodation in the interfacial region is questionable, if the molar surface tension is discussed [32]. The electrolyte solutions of various anions increase the surface tension in the following order [3]:

$$SO_4'' > Cl' > Br' > NO_3' > SCN'$$

The effects of both anions and cations depend on their hydration. The above sequence of ions is the Hoffmeister serie of ions, which is confirmed by many workers for bulk investigated by different methods.

2.4 Orientation and spreading of liquids at the interfaces

Rayleigh [37] in 1899 and Devauy [38] in 1903 pointed out that certain liquids spread out into a film one molecule thick on the surface of water, called the monomolecular film or monolayer. If a molecule with appreciable electrical moment enters the interfacial region of high order of dissymmetry, the molecular orientation seems to be evident [39]. By spreading on the air-water interface the surface active molecules orient themselves in monolayers with the hydrophilic part (such as -OH, -COOH, $-NH_2$) towards water and the hydrophobic part (such as hydrocarbon chains)

towards air [40,41].

The hydrophilic groups tend to confer water solubility, while the hydrophobic part prevents it; hence, the " hydrophilic-hydrophobic balance " (HHB) determines, whether a molecule will form an insoluble monolayer on the air-water interface. Harkins [42] considers the phenomenon of orientation and spreading in terms of " work of adhesion " and " work of cohesion ". The work of adhesion (W_a) between two liquids corresponds to the work necessary to seperate one square centimetre at the interface 'ab' into two liquid-gas interfaces 'a' and 'b' . Mathematically it can be written as,

$$W_a = \gamma_a + \gamma_b - \gamma_{ab} \quad \cdots\cdots \quad (5)$$

where γ is the surface tension. The work of cohesion (W_c) for a liquid β corresponds to the work to pull apart a column of liquid into two a/w interfaces and is given as,

$$W_c = 2\,\gamma_b \quad \cdots\cdots \quad (6)$$

Harkins [43] further pointed out that a liquid will orient and spread, if its work of surface cohesion is less, and will not spread, if its work of surface cohesion is greater than the work of adhesion. A combination of the equations (5) and (6) gives the expression,

$$S_{b/a} = W_a - W_c = \gamma_a - (\gamma_b + \gamma_{ab}) \quad \cdots\cdots \quad (7)$$

where $S_{b/a}$ is called the " spreading coefficient ".
It is obvious that a positiv value of $S_{b/a}$ corresponds to spreading , a negative value to non-spreading. Harkins [43] produced a long list of spreading coefficients for the organic liquids spread on water. One of the principal

effects of the presence of a polar group is to increase the work of adhesion. When a very polar group, such as -OH, -COOH, $-CONH_2$,-CHO etc., is present, W_a is very high compared to W_c, and hence such liquids spread.

However, a complication arises, when two substances are in contact they will become mutually saturated. For instance, if benzene is added to a water surface, a rapid initial spreading occurs, and then, as mutual saturation takes place, the benzene retracts to a lens. Harkins pointed out, that benzene has a positive initial spreading coefficient, but a negative final spreading coefficient, due to mutual saturation, contracts the benzene molecules into lens. Such behaviour of low surface tension liquids is often for water substrate.

Langmuir (53) put the spreading phenomenon in much simpler words: he considers the two surfaces of an oil film on water, an upper surface with surface tension (γ_b) and a lower surface (interface) with interfacial tension (γ_{ab}). For a stable film the surface tension of water (γ_a) should be higher than the sum of $\gamma_b + \gamma_{ab}$. He proposed the following equation in terms of spreading coefficient, which is the same as equation (7).

$$S_{b/a} = \gamma_a - (\gamma_b + \gamma_{ab}) \quad \cdots\cdots (8)$$

if $S > 0$, i.e., $\gamma_a > \gamma_b + \gamma_{ab}$, the oil spreads on water, otherwise it contracts to one or more lenses.

2.5 Surface pressure of monolayers

The most commonly measured physical property of a monolayer is surface pressure, which is defined as

$$F = \gamma - \gamma_f \quad \cdots\cdots\cdots (9)$$

where γ is the interfacial tension of clean surface and γ_f

is that of film covered surface. Measured together with the area of the film, usually expressed as area occupied per molecule, it defines the familiar F-A curve, which characterizes the physical properties of the monolayer. The surface pressure (F) can be measured by the Langmuir float method or the Wilhelmy plate method. In the Wilhelmy method the force due to the surface tension acting on a thin suspended plate partially immersed is determined, whereas in the Langmuir method a clean part of the substrate surface is seperated from the film covered area by a moveable float and the difference between the surface tensions of both parts is directly measured as force acting on the float [44]. The area available per molecule is determined by dividing the total area of the monolayer by the total number of surface active molecules. When the area per molecule is reduced by compressing the monolayer with a barrier, the surface pressure of the monolayer increases till the collapse of the monolayer (see fig.9). The pressure at collapse point is the collapse pressure and the area is the limiting area of the surface-active molecules of the monolayer.

2.6 States in monolayers

From the early studies of monolayers it became obvious that the film molecules could exist in different " states " or " phases " in the monolayers, more or less analogous to the three dimensional gases, liquids or solids. Three various monolayer states represent different degrees of freedom or order, resulting from the intermolecular forces in the film molecules and between film and subphase. The states in the monolayers and the transitions between them depend upon various factors, which may be the nature of the film molecules and particular-

ly the HHB of the film molecules, temperature, pressure and

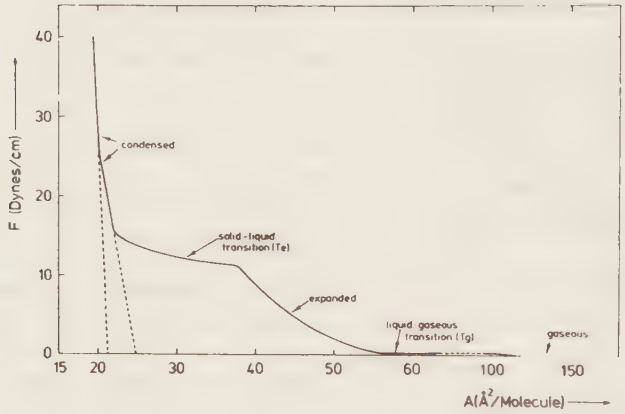


Fig. 5. Generalized F-A curve, showing various monolayer states and the transitions between them.

the subphase (see chap. 3 and 4). In table I various monolayer states, reported in literature, are summarized.

Table I: States of monolayers

Authors	Gaseous	Expanded		Condensed	
Adam[45]	gaseous	liquid expanded	transition	close-packed heads	close-packed chains
Harkins[43]	gaseous	L_1 (liq.exp.) (L_e)	I intermediate (L_e-L_c)	L_2 (liq.cond.) (L_c)	S (solid)
Dervichian[46]	gaseous	liquid	exp.meso-morphous	mesomorphous	solid

Although there is no general agreement upon the states in monolayers, these may be very useful to discuss and explain the properties of molecules spread as monolayers. To elucidate these states and transitions a general sketch of a F-A curve is given in fig. (5), in which nearly all the possible parts of curve are shown.

2.6.1 " Gaseous " state of monolayers

At larger area per molecule the monolayers of fatty acids and alcohols exist in gaseous state. The molecules in such a state of film exert very little force on one another. Such state is experimentally characterized by a larger molecular area and very low surface pressure, as shown at the extreme right of fig. (5). To measure gaseous states in monolayers an extremely sensitive apparatus is needed. Gershfeld and Pagano [47] measured palmitoleyl and oleyl alcohols, and oleic acid and stearic acid in their gaseous phases, the recorded surface pressure was between 0 and 0.15 dynes/cm. Their results are reproduced in the figures (6) and (7).

Langmuir [40] and Adam et. el. [48] treated the gaseous state on the model of the two dimensional ideal gas theory. They considered the average translational kinetic energy of 0.5 kT (k is the Boltzmann constant) for each degree of freedom of the molecules. Total kinetic energy on the surface is assumed to produce the surface pressure, which gives an ideal two-dimensional gas equation,

$$F A = kT \quad \ldots\ldots\ldots\ldots (10)$$

where F and A are surface pressure and area per molecule respectively. The equation (10) is obviously a limiting equation

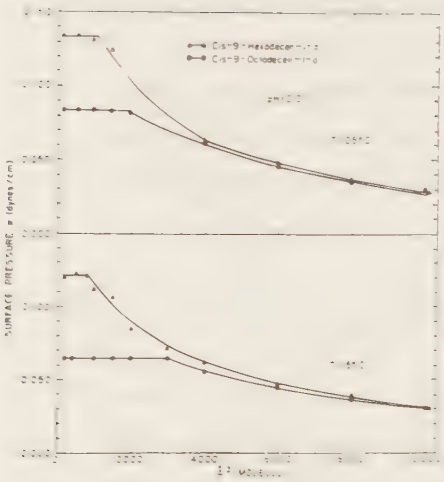


Fig. 6. F-A isotherms of palmitoleyl alcohol (▲) and oleyl alcohol (●) at 15 °C and 25 °C. (47)

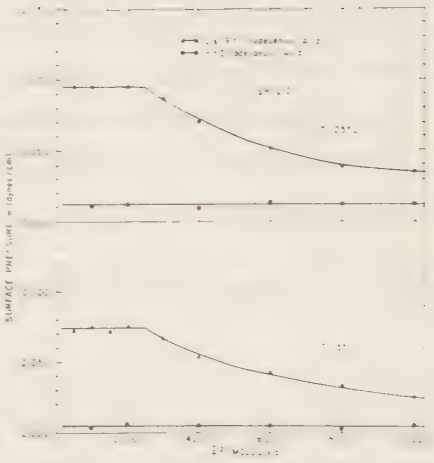


Fig. 7. F-A isotherms at 15 °C and 25 °C for oleic acid (▲) and stearic acid (●) (47)

of state for gaseous insoluble monolayers, as the three-dimensional gas equation. The derivation of the equation (10) is not convincing, because in the two-dimensional gas equation a value of 2/3 kT is expected than the given value of kT. The two-dimensional approach to the insoluble monolayers as a whole seems to be questionable, when the interactions between the hydrophilic groups of the film molecules and the underlying subphase molecules are under consideration.

2.6.2 'Expanded' state of monolayers

The film molecules in the expanded state are coherent down to relative low surface pressures, with little tendency for the film forming molecules to become widely seperated on the surface. If a monolayer shows both expanded and condensed

phases, an expanded-condensed transition (T_e) usually appears, which is shown in fig. (5).

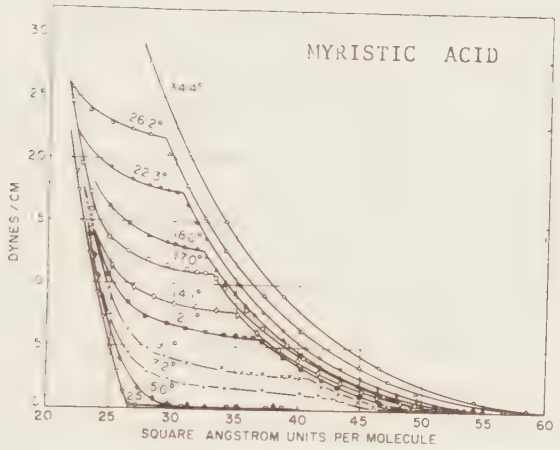


Fig. 8. F-A diagrams of myristic acid at various temperature [50].

In fig. (8) the results of Adam and Jessop [50] show the effects of temperature upon the F-A isotherms of myristic acid; the transition pressure and area is obviously temperature sensitive. Langmuir interpreted that the abrupt change in the direction of the curves (see fig. 8) must be due to the appearance of a new element in the system such as a new phase. With two phases of constant composition in equilibrium with one another, F should remain constant and curve should be a horizontal line beyond the transition point. As the experimental curves do not show a horizontal part in areas lower than the transition area, it is difficult to speak of phases at least in terms of Van der Wall's gas equation. Langmuir, however, pointed out that at such transition the chains of fatty acid molecules in the film begin to assume a close-packed arrangement in which the mole-

cules have a cross-sectional area of 20.5 $\mathring{A}^2$. The heads of the molecules cannot space themselves on the surface of the water closer than 25 $\mathring{A}^2$, because of their hydrated carboxyl group. Further compression of the film cause a squeezing-out of the water molecules until the film acquires the solid state, where all the water has been removed from the spaces between the carboxyl groups, and the chains are close-packed just as they are in crystals of fatty acids. He further sees in the new phase the presence of micelles containing relatively few molecules and the transition kink in the curves is due to the sudden appearance of the micelles at this point.

Langmuir derived the first equation of state for the expanded monolayers, assuming that the upper hydrocarbon part of the monolayer behaves as bulk hydrocarbon liquid. Thus the ideal gas equation was corrected for the surface pressure and the finite molecular size to

$$(F - F_o)(A - A_o) = kT \quad \ldots\ldots\ldots \quad (11)$$

Where F_o corresponds to the spreading coefficient for the hydrocarbon part of the film on water, and A_o is the area correction allowing for the finite size of the polar group (A_o is usually taken as the limiting area of the filmmolecule). Hedge [51] and Smith [52] proposed the improved equations for the expanded states of monolayers based upon Van der Waal's equation, which are discussed with respect to the authors result in the next chapter.

2.6.3 "Condensed" state of monolayers

The molecules stand nearly upright with their terminal polar groups in the water and the long chains closely packed

in the condensed state of the monolayers. The F-A curves are nearly straight and very steep, indicating low compressibility in the condensed monolayers [49]. Harkins [43] reported the compressibility (β) values of various substances, eg. stearic acid (C_{18}) film in solid state has the β value of 0,0009, but in the liquid-condensed state it is 0,0063 - 0,0095, whereas for the liquid-expanded state of ethyle palmitat [98] β is 0,04. This reflects the strong chain-chain interactions, which hold the molecules in their most closely-packed arrangement. In the F-A curves of mostly condensed films (eg., stearic acid or stearylalcohol) two linear segments have usually been observed (fig. 9), the lower 'liquid-condensed' (A_o - A_T) and the upper 'solid' part (A_T - A_c).

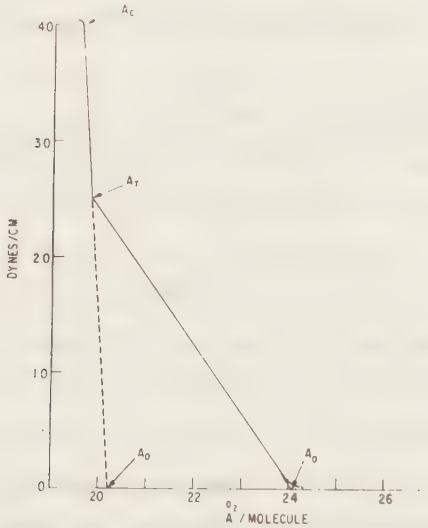


Fig. 9. The F-A curve of stearic acid at 25 °C [49].

A_o represents the extrapolated zero pressure areas, A_T is the area, where the film changes from the more compressible to the incompressible form (L_c to S form) and A_c is the area at collapse. (49)

Adam (50) suggested that the lower part of the condensed state is due to the polar 'head-contacts' between the molecules and not between the hydrocarbon chain, but in the upper part of the condensed state (solid) the molecules are close-packed chains. Langmuir (53) and Schulman et. el. (54) attributed the liquid-condensed state to the hydration of the polar group, and the reduction in molecular area in the condensed 'solid' part to the " squeezing-out " of the hydrated water molecules from the polar group.

2.7 Monolayers of nonionic surfactants

This section includes a short survey of the monolayer studies on the nonionic surfactants known in literature till now. Relatively few papers on the surface properties of nonionic detergents have appeared in literature compared to ionic detergents. The scope of investigation of the nonionic surfactants, particularly the derivatives of the ethylene oxides (EO) as insoluble monolayers is limited, since these are mostly soluble in water. This solublity problem was, however, overcome by some workers (62,68), who used the very concentrated solution (about 95%) of $NaNO_3$ or NaCl to study the ethylene oxide derivatives as spread insoluble monolayers. If the ethylene oxide groups are introduced to the long-chain aliphatic alcohols, like octadecanol etc., their insoluble monolayers on water can also be produced. Lange (62) was the first who studied the insoluble monolayers of polyoxyethylene-octadecanols (PEO)

on water and observed the expansion of the monolayers with increasing number of FO units, however, his main attention remained on soluble surfactants. Deo and Biswas et. el. [6.a] and later Shukla and Biswas et. el. [67] studied the monolayers of ethylene oxide derivatives as function of temperature and length of the hydrocarbon chain.

In order to have a complete understanding of the intermolecular interaction between FO groups of film molecules and water at interface, a comprehensive study on the monolayers of PFO is planned as function of HHB, temperature and presence of ions in the subphase. The experimental work presented in this thesis would be an extension, but also a new contribution towards the present knowledge on the surface properties of nonionic surfactants.

2.8 Surface potential of monolayers

The spreading of an insoluble monolayer leads to a permanent and measurable change in the surface potential at the interface. This observed potential difference is called the 'surface potential of the monolayer' and denoted by ΔV. The film forming molecules generally possess dipoles themselves and alter the state of the subphase liquid surface, the observed ΔV values may be a resultant of several partially compensating effects. Harkins and Fischer [55] pointed out that the surface potential is found to vary with

a) the length and shape of the hydrocarbon part of the molecule
b) the nature, number and position of the polar group
c) the hydrogen ion concentration of the solution
d) temperature
e) the concentration of the film-forming substance

f) the nature of any ions of salts present in the solution

g) time, including phenomena of hysteresis

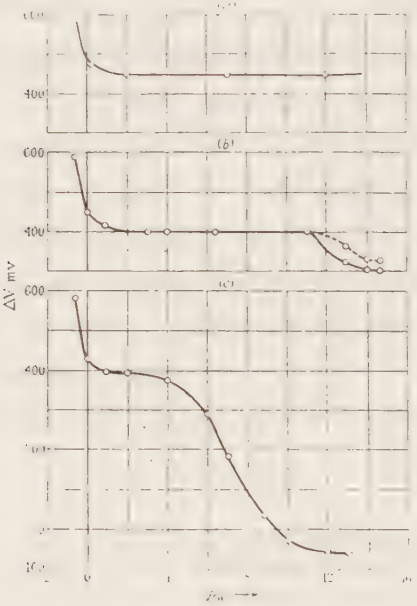


Fig. 10. The surface potentials of (a) octadecyl methyl ether, (b)tetradecyl alcohol,(c) myristic acid plotted against pH at 15 °C.(54)

In fig. (10),due to Schulman and Hughes (54), the surface potential of octadecyl-methyl-ether (a), tetradecyl alcohol (b), and myristic acid (c) are plotted against the pH of the subsolution, which casts some light on the mutual influence of the polar head group and the underlying subsolution. The sharp rise of potential on concentrated hydrochloric acid ($pH < 2$) is seen to be common to all three substances. The ether and alcohol show constant values of ΔV beyond pH=2, however, alcohol shows a marked falling-off at pH=12, but ether does not. The

behaviour of the acid is very definite, ionization of the film setting in between pH=3 and 4, with a complete reversal of sign beyond pH=9.

The surface potential of the monolayers can be compared to the potential of the ordinary parallel plate condensor [56]. A surface-active molecule has a net-electric dipole moment because of the asymmetric charge distribution among various valency bonds in the molecule. Hence, a monolayer can be considered as an array of dipoles assembled at the interface. The positive and negative charges (δ^+ and δ^-) of the dipoles are considered to form two parallel planes, seperated by a distance (d), so that $d\delta^+ = d\delta^- = \mu_\perp$ the dipole moment of the surface active molecule in the monolayer. If (m) is the number of surface active molecules per cm^2 in the monolayer (that means, m is the number of dipoles per cm^2), the surface charge density is,

$$m \cdot \delta^+ \text{ or } m \cdot \delta^- = \varepsilon \quad \cdots\cdots\cdots (12)$$

For a parallel plate condensor the potential difference between the plates seperated by a distance (d) in a medium of dielectric constant (D) is given by the Helmholtz equation [57],

$$\Delta V = \frac{4\pi\varepsilon d}{D} \quad \cdots\cdots\cdots (13)$$

where ε is surface charge density.

According to the same model the surface potential (ΔV) for unionized monolayers was given by Schülman and Rideal [58], that is $\Delta V = \frac{4\pi m\delta^+ d}{D} = \frac{4\pi m\delta^- d}{D} = \frac{4\pi m \mu_\perp}{D}$ ..... (14)

They considered the effective perpendicular moment ($\mu_\perp$) due to an interinsic moment ($\bar{\mu}$), making some angle θ with respect to the vertical, i.e., that

$$\mu_\perp = \bar{\mu}\cos\theta \quad \cdots\cdots\cdots\cdots (15)$$

Taking the dielectric constant unity they gave the following equation for unionized monolayers

$$\Delta V = 4\pi m \mu_{\perp} \quad \ldots\ldots\ldots\ldots\ldots (16)$$

Many authors [59,60,55] pointed out the severe limitations of the analogy used in developing the above equation. The reorientation of the subphase molecules contributes significantly to the observed surface potential changes, and the assignment of the unit dielectric constant is arbitrary. Gaines [49] points out that the value of $\mu_{\perp}$ evaluated from equation (17) is never the same as the interinsic molecular dipole moment of the film molecules, generally being from one-third to one-tenth of that quantity. Thus he corrected the above equation to

$$\mu_{\perp} = \frac{\Delta V \cdot A}{12\pi} \quad \ldots\ldots\ldots\ldots (17)$$

where the monolayer concentration is expressed in terms of molecular area A, in Å^2 per molecule and surface potential in millivolts.

3. Monolayers of polyoxyethylene-octadecanol (PEO) at the air-water interface

The monolayer studies of PEO at the air-water interface, particularly the force-area measurements, are of much interest, since these provide certain information about the molecular dimensions, about the interaction among the molecules of the monolayer, and about the interaction between the monolayer and the underlying substrate. The properties of the monolayers, as mentioned earlier, are mainly affected by the " hydrophilic-hydrophobic balance " (HHB) of the spreading substance, by temperature and the underlying substrate. The effects of the increasing number of hydrophilic EO units and temperature have been discussed in this chapter, while the salt effects will be covered in the subsequent chapter.

3.1 Measurements

Generally the ethyleneoxides are soluble in water and, therefore, difficult to be studied as spread monolayers with the usual Langmuir trough technique. However, their derivatives, having long-chain hydrocarbons as hydrophobic part (e.g., $C_{18}H_{37}O\ (CH_2CH_2O)_n\ H$) spread as insoluble monolayers at the air-water interface, provided n is not very large. HHB of PEO was changed by increasing the number of the hydrophilic EO units (i.e., n = 0,1,...4 and n = 9), while the hydrophobic chain ($C_{18}H_{37}$) remained unchanged.

The force-area measurements have been made upon the rectangular Langmuir's trough with a Wilhelmy balance. The sub-

phase temperature was kept constant for all the measurements (24.0 ± 0.5 °C). No pH control is necessary for the non-ionic surfactants [49], but it was noted for every experiment, which was between 5.6 - 6. The rate of compression of the monolayers was the same for all the experiments(5cm/min.).

3.1.1 Force-area (F-A) isotherms of PEO

The F-A isotherms of PEO at 24 °C are plotted in fig. 11. The condensed isotherms change into the expanded type with increasing n. The F-A curve of each substance will be described seperately in the following paragraphs.

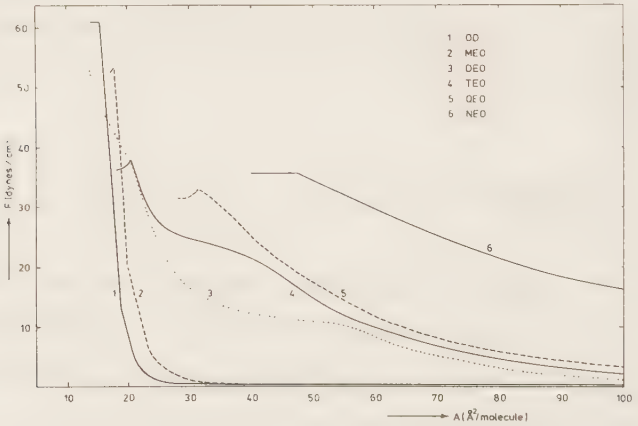


Fig. 11. The F-A curves of PEO at the air-water interface at 24 °C.

n-octadecanol (OD)

In fig. 11 the F-A curve of OD is seen as a three-phase diagram [61]. The monolayer at larger areas shows a very small pressure until the area of 25 Å^2 per molecule is reached. Here the

pressure raises slowly on further compression of the film, till a steep portion of the curve starts at 23 $\mathring{A}^2$/ molecule. This steep portion of the curve shows the liquid-condensed (L_c) part of the OD monolayer. A sharp transition between the 'liquid-condensed' and the 'solid' film (L_c-S) is observed at 19 $\mathring{A}^2$ /molecule and a pressure of 12.5 dynes/cm. On extrapolation of the liquid-condensed part to zero pressure, an area of 22.5 $\mathring{A}^2$ is found. The condensed solid part of the F-A curve starts from molecular area at 19 $\mathring{A}^2$ and collapses at 15.6 $\mathring{A}^2$ and at a pressure of 61 dynes/cm. The extrapolated area for the condensed film is 19.9 $\mathring{A}^2$, which is in agreement to the values found in literature [61,36].

Monooxyethylene octadecanol (MFO)

The curve (2) of MFO in fig. 11 resembles to that of OD (1) in its form. At larger areas the MFO monolayer shows negligibly small pressures till an area of 40 $\mathring{A}^2$ is reached and the pressure of the film raises slightly. From 26 $\mathring{A}^2$ the liquid-condensed part of the curve starts, which shows higher pressure than that of OD. The transition from liquid-condensed to solid (L_c-S) is observed at 19.8 $\mathring{A}^2$ area and 20 dynes/cm pressure. The least compressible part of the monolayer, the 'solid' state, starts at 19.8 $\mathring{A}^2$ and collapses at 17.8 $\mathring{A}^2$. The collapse pressure is 53 dynes/cm, lower than that of OD. The extrapolated area to zero pressure is found to be 21 $\mathring{A}^2$.

Dioxyethylene octadecanol (DFO)

The DFO monolayer gave a completely new form of the

F-A curve (3) than its lower homologues. A higher pressure at larger areas can be observed in comparison to OD and MFO. On compression of the monolayer the pressure increases smoothly, till a transition at 55 $\mathring{A}^2$ area and 10 dynes/cm pressure is observed. This part may be named as the liquid-expanded state (L_e). On further compression first a slow increase, but soon a rapid increase in pressure in the liquid-condensed state is noticed, till a break in the curve at 20 $\mathring{A}^2$ and 38.5 dynes/cm is reached. Instead of acquiring the solid form at this point the DFO monolayer shows an unstable region, which is in contrast to the OD and MFO monolayer. However, at 16 $\mathring{A}^2$ a sharp increase in pressure is observed again. In general this part may be assigned the condensed 'solid' state of the curve. Upon extrapolation of this part to zero pressure a limiting area of 25 $\mathring{A}^2$ /molecule has been found.

Trioxyethylene octadecanol (TFO)

The curve (4) in fig. 11 represents the F-A curve of TFO. The pressure increases smoothly on compression of the film till the L_e-L_c transition reaches. On further compression the pressure increases to its maximum, i.e. 38 dynes/cm at 20.5 $\mathring{A}^2$ in the L_c region. This is the collapse point of the film, where a sharp decrease in pressure occurs. No solid state is observed. The result corresponds with the literature values [62].

Quadrooxyethylene octadecanol (QFO)

The curve (5) of fig. 11 is the simple expanded form without any transition. This one-phase curve gives a higher pressure on the constant area than its lower homologues. The pressure increases on compression smoothly till the collapse point at 31.9 $\mathring{A}^2$ /molecule and a pressure of 33 dynes/cm is reached. The only liquid-expanded state is observed for QFO.

Nonooxyethylene octadecanol (NFO)

The F-A diagram (6) of NFO resembles to that of QFO in its shape (fig. 11). It starts, however, at a higher pressure than that of QFO. Pressure increases on compression till the curve becomes horizontal at 47.3 $\mathring{A}^2$ /molecule and 35.3 dynes/cm. The curve remains horizontal with constant pressure at lower areas. NFO does not give a sudden break in pressure at the supposed collapse point as observed in QFO and TFO films.

3.1.2 F-A isotherms of PFO at various temperatures

The monolayers of PFO have been measured between a range of 12 ^{o}C and 35 ^{o}C. The trough as well as the trough cabin was thermostated. The error in subphase temperature was ± 0.5 ^{o}C, whereas the air temperature above the monolayer was within ± 1 ^{o}C error.

MFO

In fig. 12 the force-area diagrams of MFO at three tem-

peratures (14 °C, 24 °C, 33 °C) are given. The expansion of the liquid-condensed part of the film has been observed. The turning

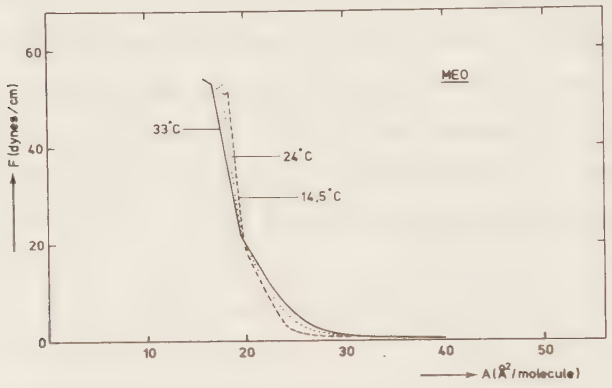


Fig. 12. The F-A curves of MFO at various temperatures.

point at lower temperature becomes diffused with increasing temperature. An increase in area can be observed at a constant pressure in the liquid-condensed range. When temperature increases, pressure increases as well, but no temperature effect is observed at large areas. On extrapolating the liquid-condensed part to zero pressure the area per molecule increases slightly with increasing temperature. The transition pressure at L_c-S transition as well as the collapse pressure increases along with the increasing temperature.

DFO

Fig. 13 gives the F-A curves of DEO at three temperatures (12.6 °C, 24 °C, 34 °C). The monolayers of DFO condense at 12.6 °C, whereas the expanded state of the monolayer is observed at 34 °C. A phase transformation at room temperature, i.e. 24 °C,

has been found at 55 $\mathring{A}^2$ and about 10 dynes/cm, which shifts towards higher area with decreasing temperature. At 12.6 ^{o}C this transition

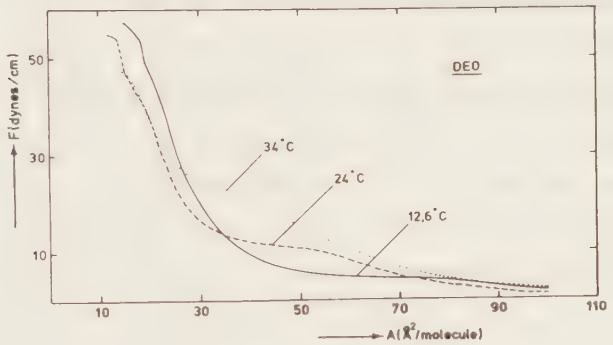


Fig. 13 The F-A curves of DEO at various temperatures

point is found at 80 $\mathring{A}^2$ and till 45 $\mathring{A}^2$ pressure does not increase rapidly on compression. At lower areas the monolayer becomes relatively stable and shows a more condensed nature at 12.6 ^{o}C. A relatively sharp L_c-S transition point at 19.2 $\mathring{A}^2$ and 49 dynes/cm is found for 12.6 ^{o}C. At 24 ^{o}C we find the same L_c-S transition and the condensed solid part as well. At 34 ^{o}C the phase transformation point is found at 40 $\mathring{A}^2$, which is the same as the transformation area of the TFO monolayer at 24 ^{o}C and 21.5 dynes/cm pressure. The temperature effect resembles with the effect of the number of EO units in the molecule. The L_c-S transition and 'S' part of the curve disappears at 34 ^{o}C.

TFO

Fig. 14 shows the isotherms of TFO, which again examplify the expanded type of monolayers. On gradual compression of the monolayer the phase transition appears as different molecular areas for various temperatures; for 13.3 ^{o}C it is 55 $\mathring{A}^2$, for 24.6 ^{o}C

it is 40 $\mathring{A}^2$, and for 34 ^{o}C there appears no such transition. For 13.3 ^{o}C the surface pressure raises rather rapidly in the liquid-condensed part from 30 $\mathring{A}^2$ till the collapse point at 21.2 $\mathring{A}^2$, whereas for 24.6 ^{o}C the rapid increase in pressure in the liquid-condensed part from 25 $\mathring{A}^2$ to the collapse point. The TFO monolayer at 34 ^{o}C gives a simple one-phase diagram, which resembles to the physical state (expanded state) of its higher homologue QEO at 24 ^{o}C. For 34 ^{o}C the collapse point is found at 25 $\mathring{A}^2$ and 38 dynes/cm pressure.

The surface tension of water decreases with increasing temperature and vice versa. The surface tension values at different temperatures are reported in table IIc, which are measured with an interfacial tensio-meter (Krüss, K 8600)

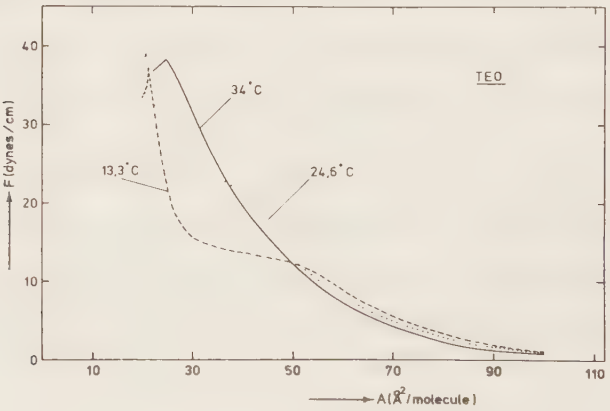


Fig. 14. The F-A curves of TFO at various temperatures.

The surface pressure of a monolayer is affected by the changes in the surface tension of water with varying temperature, since the surface pressure of a monolayer is the difference between surface tensions of clean and a film-covered surface. Therefore

it seems reasonable to correct the F-A curves at 34 °C and 13.3 °C in comparison to room temperature. In fig. 15 the corrected curves of TEO for 34 °C and 13.3 °C are shown with the original curves.

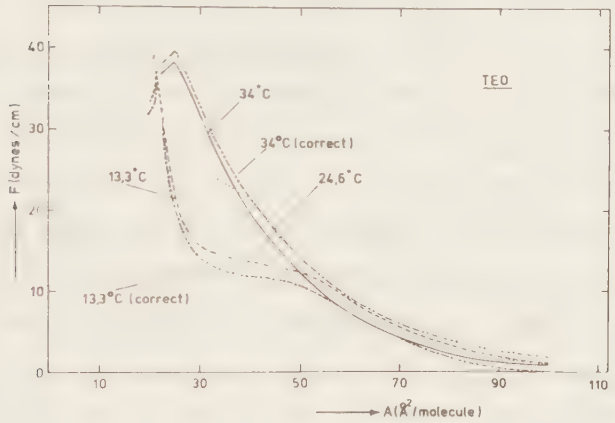


Fig. 15. The F-A curves of TEO; original and corrected curves at 34 °C and 13.3 °C for the surface tension variation with varying temperatures.

After correction the curves of TEO do not overlape each other, except at about 40 - 45 $Å^2$ where the pressure for 34 °C and 24.6 °C is the same. For every measurement at different temperatures F is always adjusted to zero before spreading the monolayer on the clean surface of water. The correction of F is justified by following equation;

$$F_{corrected} = F_{measured} + (\gamma_{24°C} - \gamma_{T})$$

3.2 Results and discussion

The force-area curves of the PEO monolayers are of much interest for the determination of the intermolecular interaction among the molecules of the monolayers as well as between

molecules of the monolayers and the underlying substrate. At very large areas there is generally weak molecular interaction, hence no appreciable pressure of monolayers can be observed. Such monolayers have been compared to the two-dimensional gaseous phases by many authors [40,48]. When the area of the film molecules is reduced by moving the barrier, a considerably higher pressure, due to the increased intermolecular interaction, can be recorded. Many names such as 'liquid', 'liquid-expanded', 'condensed' etc. have been suggested for such films by various authors (see table I). The exact classification of these so-called states of monolayers is a very controvertial matter. However, the author used the nomenclature of Harkins to specify the F-A curves of PFO monolayers.

As mentioned previously the physical states and the properties of monolayers depend upon the nature of the film molecules, particularly the hydrophilic-hydrophobic-balance (HHB) of the molecule. This has been discussed in the following sections, considering the effects of hydrophobic chains, hydrophilic groups and temperature upon monolayers.

3.2.1 HHB and monolayers of PFO

Griffin [63] devised an arbitrary scale of values to serve as a measure of HHB of surface active agents. The higher the HHB value of a surfactant, the more hydrophilic is it and vice versa. The HHB can be calculated by the equation [63],

$$HHB = 20 \frac{M}{M_h} \quad \cdots\cdots\cdots\cdots (18)$$

M_h = molecular weight of surfactant, M = share of hydrophilic group. With the increasing number of ethylene oxide units in the molecule

of octadecanol the HHB values and consequently the hydrophilicity of the whole molecule increase, whereas with lengthening of the hydrocarbon chains the HHB and the hydrophilicity of the molecule decrease.

3.2.2 Effects of the hydrophobic chains

Adam and his co-workers [48] studied the monolayers of fatty acids from C_{14} to C_{22} and found the contraction of the monolayers into condensed form with increasing length of hydrocarbon chains. In fig. 16, due to Nutting and Harkins [65], the contraction of the film with increasing number of carbon atoms (C_{14} to C_{20}) is illustrated. The contraction of the monolayers

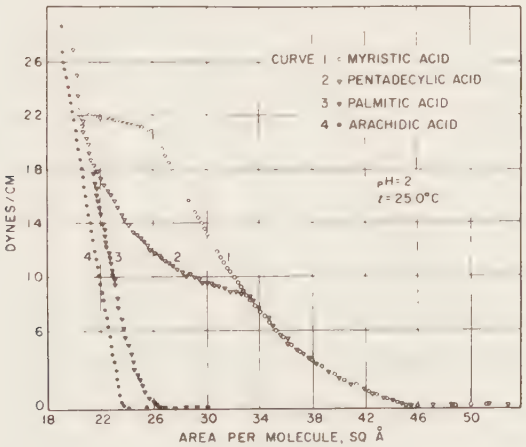


Fig. 16. The F-A curves of normal saturated fatty acids at 25 °C[65].

may be due to the higher "cohesive" forces, larger aliphatic chains in comparison to the " expansive " forces of the polar groups and water. The molecules with the larger hydrocarbon

chains may take the vertical configuration at the interface, whereas molecules with smaller hydrocarbon chains or a larger hydrophilic group may lie completely or partly flat. Lange [62] studied the monolayers of trioxyethylene-octadecanol (C_{18-3}) and trioxyethylene-dodecanol (C_{12-3}) on 5m NaCl solution, and showed that C_{18-3} has a condensed type of monolayer, but C_{12-3} gave a fully expanded film (fig. 17). He attributed the decrease

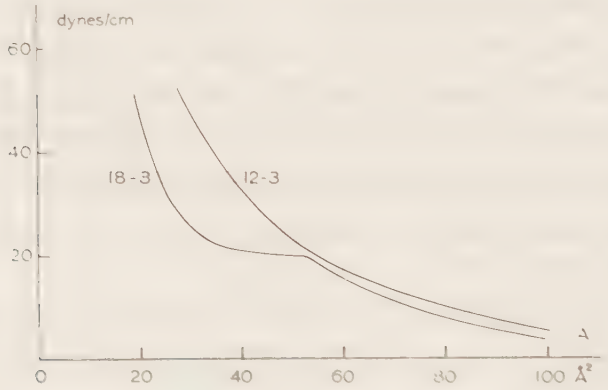


Fig. 17. The F-A curves of n-dodecanol + 3 EO (C_{12-3}) and n-octadecanol + 3 EO (18-3) on 5m NaCl (62).

in pressure and the contraction of the F-A curve of C_{18-3} to the increasing van der Waals attraction between hydrophobic groups with increasing chain length. It would be rather more clear, if we consider the increasing cohesive forces of the aliphatic chains over the expansive forces of hydrophilic groups responsible for the above effect, since HHB is reduced with lengthening of the aliphatic chains.

3.2.3 Effects of the hydrophilic group

It is of our main interest to study the influence of the underlying subphase on the physical properties of the PEO monolayers. On varying the hydrophilic group of the molecule we have a possibility to investigate the interaction between the water molecules and the polar group of the film molecules. The evident expansion of the monolayers with increasing number of ethylene oxide (EO) units, is due to increasing hydrophilicity of the PEO molecules.

The F-A curve of octadecanol (OD) (see fig. 11) is nearly straight and steep, indicating low compressibility in the condensed monolayer. This reflects the presence of strong chain-chain interaction in comparison to smaller interaction between hydrophilic groups and water, which may keep the molecules in their close-packed arrangement. The extrapolated area of the solid part of the OD curve is 19.9 Å^2, which is almost the same as the cross-sectional area (~19 Å^2) of the bulk crystal determined by X-ray measurements [66]. Adam subdivided the condensed state of F-A isotherms of alcohols (eg. curve 1 in fig. 11) into " close-packed chains ", the higher pressure region, and " close-packed heads ", the lower pressure region, while Harkins named the same regions as " solid " and " liquid-condensed " respectively (table I). The increase in the molecular area in the liquid-condensed region (22 - 23 Å^2) was suggested by Langmuir [53] and later by Schulman et el. [54] due to the hydration of the polar groups; whereas the " squeezing-out " of the water molecules by increase of surface pressure would reduce the area to that observed in more compact solid films. The ΔV-A curve of OD (fig. 27) indicates the

changes of the structure of the monolayer i.e., the existance of various 'phases', however, the OD molecules may start orienting themselves much earlier than the usually considered area of 22 $\mathring{A}^2$.

The F-A isotherm of MFO (curve 2 in fig. 11) is similar to that of OD in form, which suggests that the addition of one FO group could not make the film molecule hydrophilic enough to change the form of the curve. The molecules of MFO seem to be more hydrated than OD, since the extrapolated area of the liquid-condensed part of curve 2 is found to be 25 $\mathring{A}^2$ and the limiting area is 21 $\mathring{A}^2$. The collapse pressure of MFO is lower than that of OD. The so-called close-packed head and close-packed chain configuration, due to Adam, could also be assigned to MFO. In analogy to OD the molecules of the MFO monolayer can be considered to have vertical configuration in the condensed state. Fig. (27) shows that the surface potential of the MFO monolayer is more than OD and also the presence of different phases. The molecules may start orienting themselves at the interface earlier than 25 $\mathring{A}^2$, as the ΔV values of MFO suggest.

The expanded part of the curve of DFO (curve 3 in fig. 11, $A > 20$ $\mathring{A}^2$) suggests that " cohesive forces " of the aliphatic chains are being neutralized by the increasing " expansive forces " of the hydrophilic groups. As the HHB increased by the addition of a second ether group to OD, the interaction between the hydrophilic groups of DFO and water seems to be much increased. The appearance of the liquid-expanded (L_e) and the liquid-condensed (L_c) and a tiny solid (S) part in the F-A curve of DFO suggests, that the increasing number of FO units produces not only the increasing " expansive " forces against the cohesive forces of hydrocarbon chains, but perhaps change the configuration of

the molecules at the interface as well. The region smaller than 21 $\mathring{A}^2$ is unstable, indicates the inability of DEO molecules to be oriented vertically at the interface as the molecules of MEO and OD. Broadly, the small linear part of the F-A isotherm (curve 3 in fig. 11) between 16 and 14 $\mathring{A}^2$ may be considered as solid state, which gives an area of about 25 $\mathring{A}^2$ on extrapolation to zero pressure. This increased limiting area further supports the idea that the DEO molecule may not be vertically oriented, otherwise the limiting area must have been about 20 $\mathring{A}^2$.

The F-A curve of TFO (curve 4 in fig. 11) consists of two parts, the liquid-expanded and the liquid-condensed with the L_e-L_c transition at 40 $\mathring{A}^2$. The ΔV-A curve of TEO (fig.27) also reflects this transition, as the Δ V values increase rapidly with reducing area. For the DEO monolayer L_e-L_c transition is found at 55 $\mathring{A}^2$, but no transition is found in the QFO monolayer. Therefore, it seems reasonable to believe that some phase changes may occur at such transition, which may correspond to a change in the configuration of the molecules. The absence of the solid state and the collapse of the monolayer of TFO at lower surface pressure may be considered due to the dominance of expansive forces of hydrophilic groups over the cohesive forces.

QFO and NFO monolayers gave fully expanded, transitionless one-phase F-A isotherms (curves 5 and 6 in fig. 11). For the higher number of EO units (n =4 and 9) the expansive forces increased by increasing the interaction between hydrophilic group and water. The hydrophilic groups of QFO and NEO seem to be much stronger hydrated than their lower homologues, which induces the early collapse of both monolayers. Could the transition point be taken a measure of the reorientation of the molecules or the opening of the folded structure (may be coils, helix or meander)

of EO [68,72,73], then the molecules of the QFO and NEO would remain folded till the collapse. The ΔV-A curves of QEO and NEO (fig. 27) are almost linear functions.

3.2.4 Temperature effect upon monolayers of PFO

The monolayer of MFO is less affected by temperature as the extrapolated limiting area changes very slightly, which is about 21 $\mathring{A}^2$ (table II). The shape of the F-A curve (fig.12) is also not changed by elavation of temperature. However, in the liquid-condensed (L_c) region the monolayer expands, showing the increased molecular area at constant pressure or higher surface pressure at constant area. Langmuir [53] and Adam [45] suggested that the molecules of OD in the L_c state are hydrated and hence possess larger areas than in the solid state. With increasing temperature interaction between the polar group of the spread molecules and water molecules changes , thus the hydration of the polar groups of film molecules may change. Table IIa shows that the energy of compression(ΔE_c) (see section 3.2.8) increases with the increasing temperature.

The dominant effect of temperature upon the F-A curve of DFO is evident from fig. 13. If the break in the F-A curve of DFO is considered as indication of a phase transition, say L_e-L_c transition at 11 dynes and 55 $\mathring{A}^2$ for 24 ^oC, then this transition shifts to larger areas ($\sim$ 80 $\mathring{A}^2$) with a decrease in temperature (12.6 ^oC) and to smaller areas (40 $\mathring{A}^2$) by an increase in temperature (34 ^oC). In table IIb the values of L_e-L_c transition area are compared to those due to Shukla et el. [67]. Except for the lowest π

(12.6 °C) both results are more or less in agreement. In fig. 18 the increase of the molecular area and of the surface pressure at some constant surface pressures and molecular area is shown, where the effects of temperature on the F-A isotherms of MEO, DEO and TEO are more obvious. From fig. 18 it is clear that as the content of

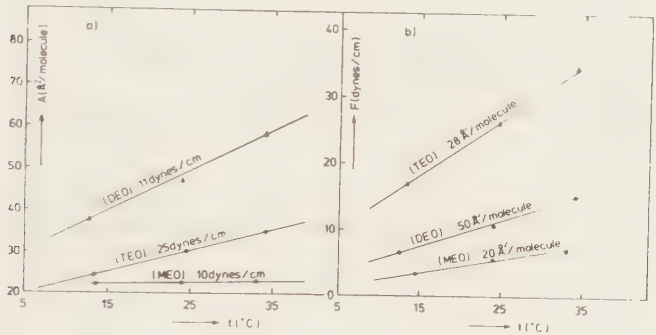


Fig. 18. (a) molecular areas of MEO, DFO and TFO against temperature at definite surface pressures; (b) surface pressures of MEO, DEO, and TFO against temperature at certain molecular areas.

free -OH groups in water increases with increasing temperature [1], the area per molecule at constant F and pressure at constant A increases, causing the expansion of the monolayers of PFO.

Fig. 14 shows that, at larger areas temperature has little but reverse effect than at smaller areas of the TFO monolayer. However, this reverse effect is overcome by correcting the F-A curves of TFO at 13.3 °C and 34 °C in comparison to 24.6 °C in fig. 15. The correction of the curves is found necessary, because the surface tension of water decreases with increasing temperature, as shown by the values given in table IIc. The shifting of the L_e-L_c transition in the TFO isotherm is observed with varying temperature, as shown by the L_e-L_c transition pressure

and area values produced in table IIc and compared with the literature [62, 67]. Shukla et el. [67] reported a little higher

Table II: Molecular area (A); surface pressure (F); L_e-L_c transition; energy of compression (ΔF_c) of DFC monolayers and surface tension of water (γ) at various temperatures (t).

(a) MFO:

temperature (t)	A at 4 dynes/cm	extrapolated limiting A	F at 24 $Å^2$ / mol.	ΔF_c
^oC	$Å^2$/ mol.	$Å^2$ / mol.	dynes/cm	erg/mole
14.5	23.7	20.9	3.3	$0.107 \cdot 10^{10}$
24.0	24.8	21.0	5.7	$0.118 \cdot 10^{10}$
33.0	25.8	21.3	6.9	$0.123 \cdot 10^{10}$

(b) DFO:

(t)	ΔF_c	L_e-L_c trans.A	L_e-L_c trans. F	literature (67)		
				t	A (L_e-L_c)	F (L_e-L_c)
^oC	erg/mole	$Å^2$/mol.	dynes/cm	^oC	$Å^2$/mol.	dynes/cm
12.6	$2.15 \cdot 10^{10}$	80	4.4	15	65	4.6
24.0	$2.23 \cdot 10^{10}$	55	10.5	25	53	10.8
34.0	$4.38 \cdot 10^{10}$	40	21.5	35	39	20.0

(c) TFO:

(t) ^oC	γ dynes/cm	ΔF_c erg/mole	A at 25 dynes/cm	F at 25 $Å^2$	L_e-L_c A	L_e-L_c F	literature		
							t ^oC	L_e-L_c A	L_e-L_c F
13.3	73.7	$2.27 \cdot 10^{10}$	24.2	22.0	55	12.0	15	50	16
24.6	71.8	$3.25 \cdot 10^{10}$	30.0	28.2	40	21.2	25	40 (67) 40 (62)	26 (67) 21.5 (62)
34.0	70.4	$2.53 \cdot 10^{10}$	35.0	38.0	-	-			

pressure than ours, whereas the values for the molecular areas are nearly in agreement. Our results, moreover, agree with those reported by Lange [62] at room temperature. The energy of compression (ΔF_c) reported in table II is calculated from the integral area of the F-A diagams, which are influenced by the kT energy as well as by the hydration of the PEO molecules. As the temperature varies, the energy of compression changes too. However, it is difficult to discriminate the effects of kT and of hydration, because both are associated with each other. Further it was not aimed in present work.

3.2.5 HHB and temperature effect

It has been observed that the F-A curves of PEO at one temperature expanded with the increasing number of ethylene oxide units, i.e., by increasing HHB values or the increasing hydrophilicity of the PEO molecules. The increase in temperature has shown some common effects with the HHB effects upon the PEO monolayers. Fig. 19 shows that the F-A curve of DEO at 34 ^{o}C resembles the curve of TEO at 24 ^{o}C, the L_e-L_c transition is found at 40 $\mathring{A}^2$ for both isotherms. Further, the F-A curve of TEO for 13.3 ^{o}C resembled that of DEO at room temperature (fig. 19b). Though the values of pressure of both curves are not the same, the L_e-L_c transition is found at the same area, 55 $\mathring{A}^2$. On elevating the temperature to 34 ^{o}C a transitionless one-phase F-A isotherm is obtained, which resembles to the QEO isotherm at 24 ^{o}C (compare fig. 14 with fig. 11).

It could now be postulated that the elavation of temperature increases the extent of hydration of the EO units, and hence the configuration of EO. The variation of degree of hydration could be attributed to the structure of water, which is

sensitive to the temperature (see part I). By elevating the temperature the number of free -OH bonds of water increases, enabling the PEO molecules to be strongly hydrogen-bonded with the

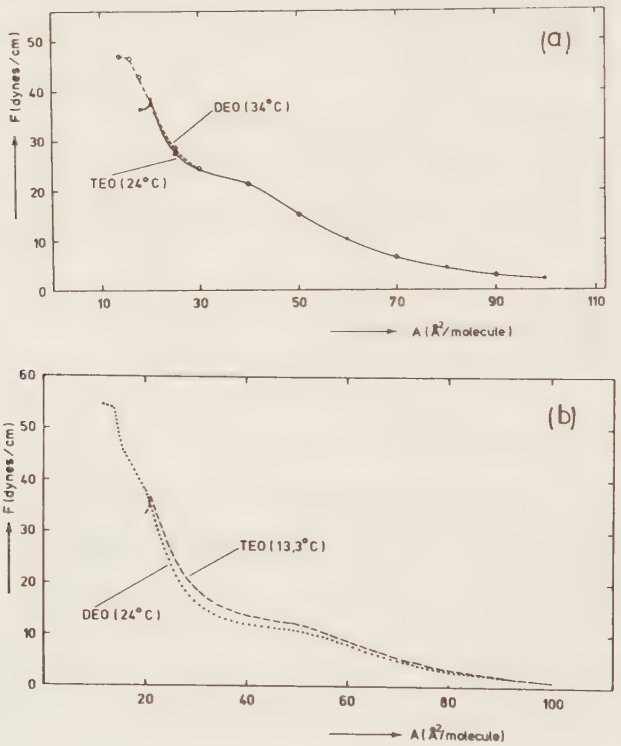


Fig. 19. (a) The F-A curves of DEO and TEO at 34 °C and 24 °C respectively, (b)the F-A curves of DEO and TEO at 24 °C and 13.3 °C respectively.

underlying water. Thus the increasing hydration of PEO may influence the configuration of the EO. Instead of possible one-ring meander form [73] for DEO at room temperature, for example, a two-ring meander structure could appear at 34 °C resembling to the TEO configuration at room temperature.

If the coiled[68] or helix type [72] configuration of EO is considered, the size of such coils or helices in case of 34°C for DFO have increased to that of TFC at 24.6 °C as fig. 19 suggests. If this idea should be accepted, the consequence would be the pulling of the hydrophobic chain partly into the underlying water for higher temperatures and reverse for the lower temperatures. Similar considerations have been made by Heusch [64] and Becher [69] for the polyglycol ethers with varying hydrophilicity.

It is known that the lengthening of hydrocarbon chains has a similar effect as the decreasing of temperature, i.e., the condensation of monolayers [65]. The author showed that the lengthening of the hydrophilic part by EO units has similar effects as the increasing temperature, the expansion of the monolayer. The elavation of temperature by about 10 °C shows the similar effect as the increasing of one ethylene oxide unit.

3.2.6 Equation of state for expanded monolayers

The range of stability of various atates of the monolayers of the same substances at various temperatures change in a regular order, which may be analogous to the pressure-volume-temperature behaviour of ordinary three-dimensional phases [53]. A number of attempts have been made to develop the equation of state to apply on monolayers by many authors, starting with Langmuir [53], who stated the following equation

$$(F - F_o) (A - A_o) = kT \quad \text{.....(19)}$$

In the equation 19, F and A are surface pressure and surface area respectively, A_o is usually taken limiting area of the film molecules, k is the Boltzman constant and T is the absolute temperature.

Langmuir considered the hydrocarbon tails as a layer of oil with spreading pressure F_o and the carboxyl head groups to act as an imperfect two-dimensional gas. The assumption of a normal oil like portion and a gaseous polar head portion is rather forced and seems particularly unwarented in view of the anomalously high viscosities of the liquid-expanded phases [35].

Hedge [51] proposed an equation of state for liquid-expanded monolayers, based upon the van der Waals equation for imperfect gases,

$$\left(F + \frac{a}{A^2} \right) \left(A - A_o \right) = kT \quad \ldots\ldots\ldots\ldots \quad (20)$$

Here (a) is the attraction constant. All other terms are the same as for equation 19.

Smith [52] considered this equation suitable for gaseous state, but not for the liquid-expanded state. He modified the above equation, considering the molecules to be like stacks of hard disks (CH_2 groups) of diameter d, anchored to the water by the head group. His equation of state reads,

$$\left(F + \frac{a}{A^2} \right) \left[A \left(1 - \frac{A_o}{A} \right)^2 \right] = kT \quad \ldots \quad (21)$$

where the attraction constant $a = m\varepsilon A_o$; m is the number of the CH_2 groups and ε is the potential energy when two disks touch each other. The correction $\left(1 - \frac{A_o}{A} \right)^2$ is taken from a statistical mechanical treatment of a two-dimensional fluid

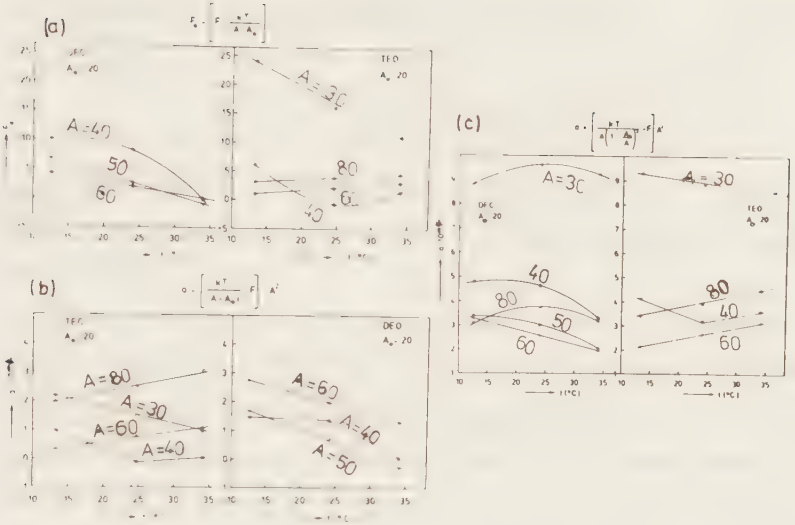


Fig. 20. The constants of (a) Langmuir's equation; Hedges equation(b) and (c) Smith's equation calculated for DFO and TFO monolayers, plotted against temperature for different molecular areas.

of hard disks[70]. Smith considered the polar head group just another disk in the stack.

From the experimental values of the F-A diagrams of DFO and TFO the constants F_o, and a, have been calculated using A_o=20 Å^2, the collapse area, and are plotted against T in fig.20. The value of F_o, calculated from eqn.19, is constant neither for different molecular areas nor with varying temperature (see fig.20 a). Similarly the calculated values of constant 'a' from eqns.20 and 21 change with temperature as well as for different molecular areas at same temperature (see figs. 20 b and c). The poor agreement of the constants (F_o,a) calculated from different equations show that the selection of A_o=20 Å^2 as collapse area or extrapolated area at F=0 is not suitable. The extrapolation of the area at T=0^oK may give the correct value of A_o.

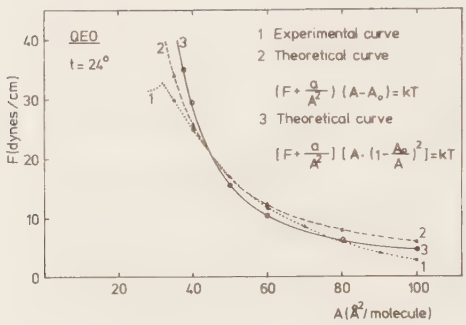


Fig. 21. The F-A curves of QEO: (1)experimental,(2)theoretical from equ.20, using $a = -8.2 \cdot 10^3$; $A_o = 20$ Å²/mol., (c) theoretical from equ.21, using $a = 1.88 \cdot 10^4$; $A_o = 20$ Å²/mol.

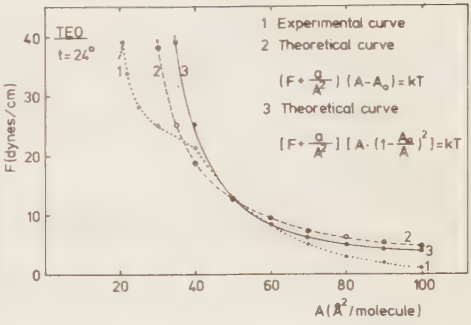


Fig. 22. The F-A curves of TEO: (1)experimental, (2)theoretical from equ.20, using $a = 0.28 \cdot 10^3$; $A_o = 20$ Å²/mol., (c)theoretical from equ. 21, using $a = 2.56 \cdot 10^4$; $A_o = 20$ Å²/mol.

Though the values of 'a' and A_o are not found absolutely constant, the theoretical values of F have been calculated by equ.20 and by equ. 21. The theoretical values of F are plotted against A as F-A isotherms along with the experimental isotherms of QEO and TEO in figs. 21 and 22 respectively. The theoretical curves are found more or less in agreement with the experimental curve of QEO(figs.21). For the liquid-expanded part ($A > 40$ Å²/mol.) of TEO curve the agreement in experimental and theoretical values is also not too bad, but in the liquid-condensed part ($A < 40$ Å²/mol.) there does not appear an agreement. The L_e-L_c transition at $A = 40$ Å² could not be produced in the theoretical curves of TEO. In principle the kink in F-A curves could be detectible, at least mathematically, by selecting the fitting values of the constants 'a' and 'A_o'. However, at this stage the applicability of above equations on liquid-expanded isotherms is to be considered.

3.2.7 Hydration and intermolecular interaction

Only a slight increase in the molecular area is observed on addition of one EO unit to octadecanol, but a rapid increase is observed in the expanded regions, e.g. at 12 dynes/cm and 20 dynes/cm, when further units of EO are added (see fig. 23a). In the condensed state (e.g. 30 dynes/cm) the molecular area increases linearly upto 3 EO units, indicating the partly dehydrated condensed monolayer state, but OEO (n =4) retains still much larger area reflecting the strong hydrated sphere of water around the hydrophilic group of OEO. The hydrogen-bond formation between EO and water molecules seems to be mechanism of this hydration. The more the number of EO units in the molecule, the more water would be attached to the PEO molecules. This could change the orientation and configuration of PEO molecules at the interface.

With the increasing number of EO units the intermolecular interaction between the film molecules and water molecules increase. This increases the surface pressure of the PEO monolayers, since the expansive forces of hydrophilic groups dominate the cohesive forces of the hydrophobic chains. In fig. 23b three molecular areas are considered where the alphatic chain of 18 carbon atoms has almost negligible contribution to the surface pressure (i.e. n=0). The pressure increases due to increasing interaction between hydrophilic groups and water molecules with increasing number of EO groups. At very large areas (e.g. 100 $Å^2$) where the intermolecular interactions are very small, the increase in pressure with increasing EO units is also very small. It has been shown in fig. 23b that one EO unit has no significant effect

upon surface pressure at smaller areas (e.g. 40 or 32 $Å^2$), but further addition of EO units increase the pressure tremendously. This may indicate also that 1 EO group is not sufficient to change the vertical configuration of octadecanol [45]. The PEO molecules with higher number of EO may acquire a somewhat coiled [68] or meander [73] type of configuration (see section 3.2.9).

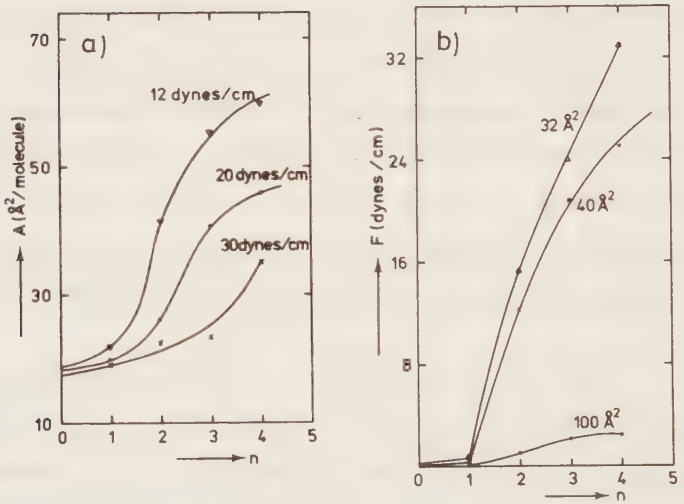


Fig. 23 (a) molecular areas plotted against the number of EO units (n) at three different surface pressures at 24 °C, (b) the surface pressures for PEO for three molecular areas vs (n) at 24 °C

The opening of such folded structure may need more energy, which is observed in form of higher surface pressure with increasing n. It could also be argued that the hydrophilic groups of higher members of PEO are more strongly hydrated than the lower members, therefore the former exert more pressure than the latter.

3.2.8 Energy of dehydration

How does the increasing number of hydrophilic groups of an uncharged film contribute to the surface pressure of a monolayer?

Gaines [71] regards this question as one of the unsolved problems. The hydration of the hydrophilic group of PFO molecules takes place by the hydrogen bonds, since the ethylene oxides are well suited for hydrogen bond formation with water [1]. The orientation of water molecules around the hydrophilic group becomes under stress, when the monolayer is compressed towards smaller areas. Due to the compression of the monolayer the molecules are reorientated at the interface, and the water molecules are forced out of hydrated sphere around the hydrophilic group [53]. This may be called the 'dehydration' of the hydrophilic part of the film molecule. Free energy of compression represents the work required to compress the gas film to some condensed state [47]. It can be assumed that the film molecules exert an equivalent counter force to retain their hydrated sphere of water against the energy of compression. Should the film molecules retain the same content of water of hydration as before compression, the energy used by the film molecules against the energy of compression may be named as " energy of dehydration (F_d) ". It should be pointed out that the contribution to ΔF_c (eq.22) is from kT, and aliphatic and polar part of the film molecules. Since the hydrophobic part ($C_{18}H_{37}$-) is common for all the PFO molecules and only the FO units vary, ΔE_c may give us a good relative measure to study the interactions of hydrophilic group and subphase. The ΔE_c has the components of intermolecular interaction among the polar groups of film molecules and between polar groups and water molecules, and energy of kT, i.e.,

$$\Delta E_c = F_d + F_{kT} + F_{hydrophob}$$

The Helmholtz free energy of compression [47] (ΔE_c) can be evaluated from the experimental F-A isotherms by the following expression:

$$\Delta E_c = E - E_i = - \int_{A_i}^{A_c} F \cdot dA \quad \ldots\ldots\ldots\ldots (22)$$

where E is energy of the film in a condensed solid state at the molecular area A_c, E_i is the energy in the gas or liquid state, at the molecular area A_i. In fig. 24 the integrated area of the

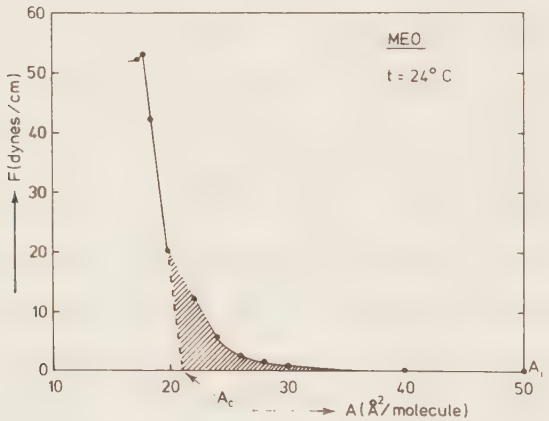


Fig. 24. The integrated area of the F-A curve of MEO between the area of expanded state A_i, and area of condensed state A_c.

F-A curve of MEO is shown between A_i, area at expanded state, and A_c, molecular area or solid state i.e. the limiting area of MEO, which gives the free energy of compression or energy of dehydration of MEO monolayer.

In fig. 25 the energy of dehydration (E_d) is plotted against the number of ethylene oxide units. A slight increase in E_d for 1 EO unit but an abrupt increase in E_d for higher number of EO units is seen from the fig. 22. QEO shows less values than

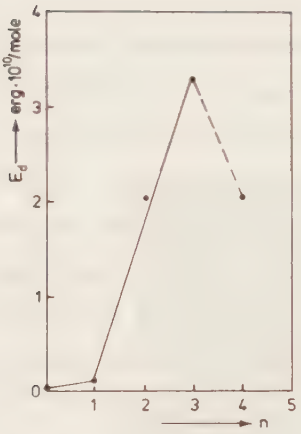


Fig. 25. The energy of dehydration (F_d), calculated from the F-A curves of PEO at 24 ^{o}C, plotted against the number of ethylene oxide units (n).

T F O because the film collapses. The smaller F_d value of QEO than TEO appears to be due to the fact, that the integrated area for F_d was calculated from the collapse point of the QEO isotherm, since the latter did not show any condensed state. It may be suggested that for the more hydrated monolayers more energy of compression would be needed to bring their molecules in the close-packed condensed state, where the molecules are supposed to be almost dehydrated or at least partly. Thus the extent of hydration of the monolayer may be an appropriate answer to the above question, i.e., the contribution of hydrophilic groups to the surface pressure. The energy of dehydration of PEO at various temperatures (table II) supports the above idea. With increasing temperature E_d values become larger, indicating the stronger hydration of hydrophilic groups of PEO molecules for higher temperatures.

3.2.9 Configuration of PEO molecules

According to the orientation of molecules at interfaces it is obvious that the hydrophobic group of PEO would remain above and the hydrophilic group beneath the air-water interface. There could be a number of possible configurations of the ethylene oxide chains at the interface, for instance they may stand as vertical cylinders in the subphase, may lie flat at the interface or may acquire some disordered folded structures in the form of ether coils [68], helix [72], or meander [73] configurations.

Since octadecanol (n=0) gives only a condensed type of film, it has been assigned a vertical configuration in its condensed state [45,49]. At the larger areas molecules of OD may lie flat at the interface, but would reorient themselves vertically when compressed to smaller areas [49,53]. MEO (n=1) gives a similiar type of F-A curve as OD, which is quite in agreement with the literature values [36,61]. In analogy to OD it is appropriate to consider the MEO molecules oriented vertically at the interface. It may have a zig-zag (that is -OH in trans) configuration.

Staudinger [73] postulated two configurations for the ethylene oxide chains in water, " zig-zag " and " meander ". On the basis of solution viscosity and melting point data he pointed out the meander configuration more favoured one. He attributed, moreover, the chain contraction of polyethylene oxide to the increase in intermolecular attraction of the ether oxygen with increasing degree of polymerisation. Another likely reason for the chain contraction of EO may be the orientation of water molecules at the ether oxygen atom or the hydration of EO, since the ethylene oxides are well known to form hydrogen bonds with water[1].

As is discussed in previous sections that the hydration of the PEO molecules increases with increasing number of EO units, some disordered folded structure (may be coils, helices or meander form) of EO chains for the higher members of PEO could be expected.

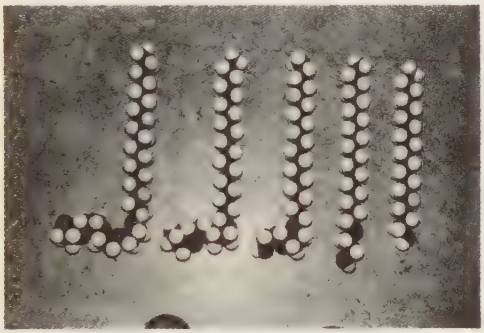


Fig. 26. The molecular models of PEO (n= 0,1...4) showing the possible vertical configuration of OD and MEO, and folded or coiled form for DEO, TEO, and QEO molecules in the monolayers at the interface.

The force-area curves of DEO, TEO and QEO and also NEO are completely different from those of OD and MEO(fig. 11). The absence of the condensed solid part in the F-A curves of former indicates that the EO may not be vertically oriented, but remain somewhat folded till the collapse of the monolayer. Schick [68] studied octadecanol with long EO chains on 95 % saturated sodium nitrate solution and concluded the coiled form for EO chains. In fig. 26 a photograph of molecular models of PEO (n= 0,1,2,3,4) is shown with the possible vertical configuration of OD and MEO, and folded or coiled form of the EO part of the molecule of DEO, TEO, and QEO.

Thus it now can be concluded that the molecules with smaller hydrophilic groups (eg. -OH or OC_2H_4OH) may acquire a vertical configuration and give a condensed type of film. On the other hand, the molecules with the larger hydrophilic groups, such as two or more EO groups, give the expanded films, their EO groups may form some folded structure which could be coiled, helix or meander type of configuration. The changes in the F-A curves could be induced by increasing interaction of water-ether groups too.

3.4 Surface potential of PEO monolayers

Despite the fact that the interpretation of monolayer surface potentials is very difficult, measurement of the surface potential can provide useful information. Inhomogeneities of monolayers can be detected. Monolayers of ionized and of uncharged molecules can be discriminated, and the changes in the monolayer due to phase transitions or chemical reactions can be investigated [44]. The investigation of surface potential (ΔV) of PEO, particularly the contribution of number of ethylene oxide to ΔV is presented in this section.

3.4.1 Surface potential measurements

The surface potential measurements have been carried out with the vibrating plate electrode method on a circular teflon trough. All the measurements have been performed under similar experimental conditions. Experimental details are given in chapter 5. The ΔV-A curves of PEO are given in fig. 27.

ΔV - A curve of OD

At the larger areas (A > 50 Å^2) the monolayer of octadecanol has a constant surface potential of ΔV = 64mV. On compression at 50 Å^2 the surface potential increases sharply, but from 40 Å^2 on the increase in ΔV is not so rapid, but rather smooth. The maximum potential observed is 380-385 mV. The existance of various monolayer phases and the reorientation of the molecules of the monolayer can be predicted from the OD curve in fig. 27.

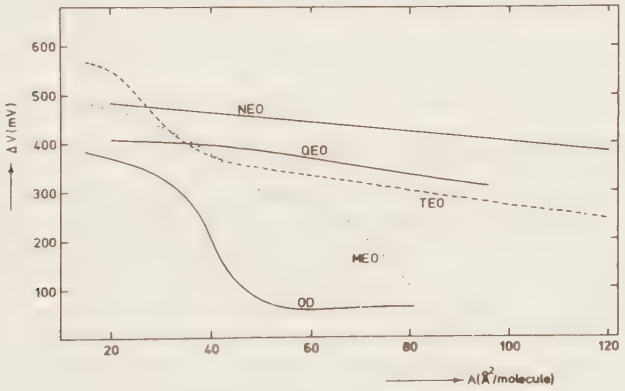


Fig. 27. The ΔV - A curves of PFO at the air-water interface at 25 °C.

ΔV - A curve of MFO

The ΔV - A curve of MFO (fig. 27) shows the increase in surface potential of the MFO monolayer upon compression from larger to smaller areas. Between A=65 and A=55 Å^2 a nearly constant potential is observed (ca. 200 mV). On further compression the potential increases again sharply. A slow increase in potential is observed in smaller areas of the monolayer and at collapse the

maximum potential is reached to 480-490 mV.

ΔV - A curve of TFO

On compression of TFO monolayer to smaller areas a linear increase in ΔV is evident from fig. 27. An obvious change in the pattern of ΔV-A curve is seen at 40 Å^2, where the phase transition has been noticed in the F-A curve of TFO. From this point onwards the surface potential increases rapidly till the collapse point ($\sim$20 Å^2).

ΔV - A curve of QFO and NFO

The increase in surface potential on compression of both monolayers is almost a linear function of the molecular area as shown in fig. 27. Both monolayers are fully expanded and transitionless, hence no discontinuity in their V-A curves is found. In the smaller areas the potential values of QFO are less than that of TFO and MFO, while NFO has less values than TFO. In such molecular areas both QFO and NFO monolayers are collapsed and no new phase appeared.

3.3.2 Surface potential and dipole moments of PFO

Davies and Rideal [56] considered three major contributions to the surface potential of a monolayer; the dipole moment of a polar group of film molecules, μ_1; the reorientation of water dipoles, μ_2; and the dipole moment of the terminal methyl group of hydrocarbon chain, μ_3. Thus the Helmholtz equation can

be written in the following form,

$$\Delta V = 4 \pi m \mu_D \quad \ldots\ldots\ldots\ldots\ldots \quad (23)$$

where $\mu_D = \mu_1 + \mu_2 + \mu_3$ and (m) is the number of the film forming molecules pro cm^2 (see also section 2.8).

In the comperative Δ V-A measurements of PEO with a constant hydrophobic group ($C_{18}H_{37}$-) under similar experimental conditions the changes in surface potential of PEO monolayers may be considered due to the varying number of polar groups and the reorientation of water molecules around them. With the increasing number of hydrophilc groups (EO) the surface potential increases. For two molecular areas A = 50 and A = 70 $\mathring{A}^2$ the surface potential (Δ V) has been plotted in fig. 28, a sharp increase in Δ V compared with OD is seen for the first EO group and further EO units show a smaller increase. In the Δ V-A curves of OD, MEO and TEO in fig. 27 there are certain "discontinuities" and turning points, which may correspond to the transitions of the phase or state changes of these substances. On the other hand the Δ V-A curves of QEO and NEO show only linear increase in ΔV, but no breaks or kinks indicating the absence of phase transitions in their monolayers. At smaller areas, say 25 $\mathring{A}^2$, the ΔV values of QEO and NEO are less than TEO and MEO, respectively (fig. 27). It should be remembered from the F-A curves that the molecules of the lower homologues, MEO and TEO are still orienting further in their condensed state, whereas the QEO and NEO monolayers are already collapsed at the above mentioned area.

Schick [74] pointed out that the dipole moments of soluble polyglycol ether of dodecanol increase with increasing number of EO, who studied them as adsorbed films. The author found a similar increase in the dipole moments of PEO with increasing number of EO units, as shown for two molecular areas in fig. 29.

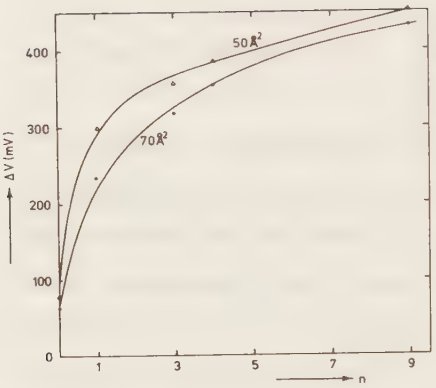


Fig. 28. Surface potentials of PFO monolayers at 25 °C plotted as a function of number of FO units (n) at 50 Å² and 70 Å² per molecule.

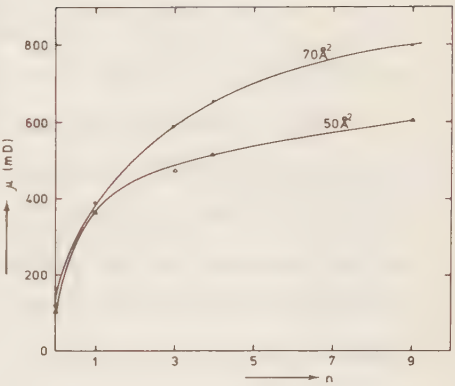


Fig.29. Dipole moments of PEO, calculated from V-A curves at 25 °C for molecular areas of 50 and 70 Å², plotted as function of FO units (n).

The dipole moments are calculated from the ΔV-A curves of PFO using the Helmholtz equation (equ. 23), which holds for any electrically neutral film containing dipoles [58]. Though the application of the Helmholtz equation is very controversial, it has very often been used to calculate the dipole moments of other monolayer molecules [74,75].

3.3.3 Correlation between F-A, ΔV-A and μ-A curves of TFO

In fig. 30 a correlation between F-A, ΔV-A and μ-A curves of TFO has been shown. The F-A curve shows two phases of the TFO monolayer expanded and condensed, with a transition point at 40 Å².

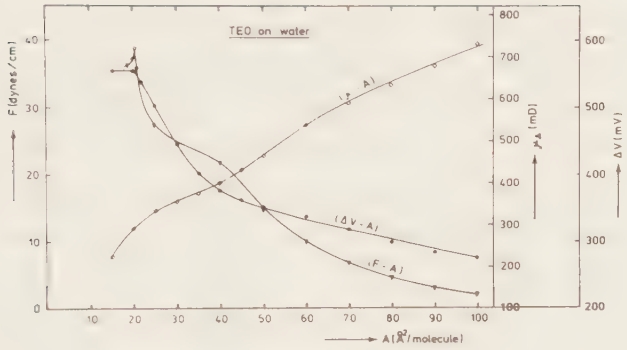


Fig. 30. The F-A, ΔV-A, and μ-A curves of TFO at 25 °C.

The surface potential of TFO first increases smoothly on the compression of the monolayer, but at about 40 $Å^2$ the potential increases sharply, thus seperating the ΔV-A curve into two parts. These two parts of the ΔV-A vurve may be regarded as representing the two phases of the monolayer found by the F-A curve. In contrast to the potential values the dipole moments ($\mu_\perp$) of TFO decreases on compression of the monolayer. A turning point at about 40 $Å^2$ is found in ΔV-A curve as well, indicating the transition point between two phases of the TFO monolayer. The collapse point of both F-A and ΔV-A curves appear to be same.

4. Monolayers of PFO on aqueous solutions[95]

The effects of salts in bulk water are well known (see section 2.2), for example, the anions are known to have stronger effects than the cations[26]. On the critical micelle concentration of polyethylene oxide derivatives the anions show much larger effects than the cations[26]. Relative to ionic monolayers very little is known about the effects of anions on the insoluble monolayers of nonionic surfactants. Lange[96] studied the effects of NaCl on the monolayer of n-dodecanol-ethyleneoxide. Ralston and Healy[36] investigated the effects of cations on the monolayer of octadecanol.

In the present work the effects of various anions on PFO monolayers are discussed in terms of "structure-makers" and "structure-breakers", and compared with the effects of salts on the water properties in bulk. The salt effects on PFO monolayers are further correlated with the "structural temperature" of respective aqueous solutions.

4.1 Measurements of F-A isotherms of PFO on aqueous solution

The isotherms (F-A) of monolayers of PFO have been measured on various electrolyte solutions like Na_2SO_4, NaCl, $NaNO_3$ and $NaClO_4$. The experimental conditions have been kept constant for all the measurements. The surface pressure F is always adjusted to zero for the salt solution without film. The surface tension of the investigated aqueous solutions (1m) are measured with an interfacial tensiometer (table III).

4.1.1 The F-A isotherms of OD and MFO (condensed)

In fig. 31 the F-A isotherms of OD on various substrates are given . The addition of salts to the subphase causes

an expansion of the condensed OD monolayer. The most affected part of the F-A curve is the liquid-expanded (l_e) and liquid-condensed (L_c).

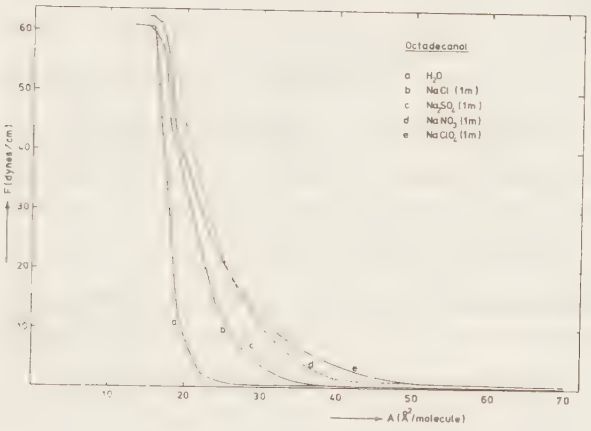


Fig. 31 The F-A isotherms of octadecanol on various electrolyte solutions at 24 °C.

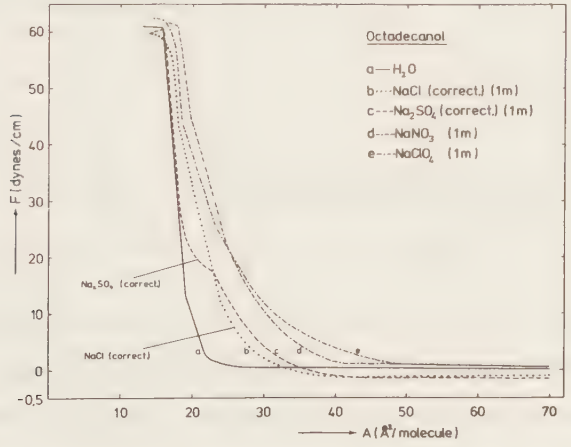


Fig. 31a. The F-A isotherms of OD on various aqueous solutions at 24 °C including the surface tension corrected curves on Na_2SO_4 and NaCl

in the solid region of the isotherm the monolayer is expanded slightly. In the expanded region, e.g., at a low pressure of 5 dynes/cm, the expansion of the monolayer due to various anions increasing in the order:

$$H_2O < Cl' < SO_4'' < NO_3' < ClO_4'$$

The position of SO_4'' in this series is not in agreement with the Hoffmeister [7] series of anions, and also not parallel to their effects on the surface tension of water as seen from the values in table III.

Table III. Molecular areas (A), surface pressures (F) of OD on various aqueous solutions (1m) of surface tension (γ) at 24 °C. (tr.A = transition area ; tr. F = transition pressure)

sub-strate (1m)	γ at 25 °C	A at 5 dyn/cm	L_e-L_c tr.A	L_c-S tr.A	L_e-L_c tr.F	L_c-S tr.F	extrap. L_c. A	extrap. S. A
	dyn/cm	$Å^2$/mol	$Å^2$/mol	$Å^2$/mol	dyn/cm	dyn/cm	$Å^2$/mol	$Å^2$/mol
H_2O	71,75	21,2	22,5	19,0	2,3	12,5	22,5	19,9
Na_2SO_4	74,1	32,3	23,0	-	19,8	22,0	-	20,0
NaCl	73,2	29,0	24,0	18,0	14,0	44,0	27,0	21,2
$NaNO_3$	71,8	34,5	25,0	21,0	21,6	44,0	30,0	23,0
$NaClO_4$	71,6	38,3	25,0	20,0	22,0	43,8	31,0	23,0

Since the surface pressure (F) is the difference between interfacial tension of aq.solution without film and film covered surface, it appears necessary to correct the F values for various aqueous solutions according to the surface tension of pure water. In fig. 31a the F-A isotherms of OD on Na_2SO_4 and NaCl solutions are corrected by comparing their surface tension values with that of

water. The surface tension of $NaNO_3$ and $NaClO_4$ solutions is not much different from water (table III), hence no correction was needed. Despite the correction in surface pressure of curves (b) and (c) the anionic series remained as above. Sodium sulphate further shows a complicated behaviour at the L_c-S transition, which is smooth and has no sharp kink.

From table III it is evident that for $NaClO_4$ the transition between liquid-expanded and liquid-condensed phases (L_e-L_c), and the extrapolated liquid-condensed (L_c) and solid (S) areas are larger than in the case of other salts and particularly than sulphate. On sodium sulphate the limiting solid area of OD is similar to that on water.

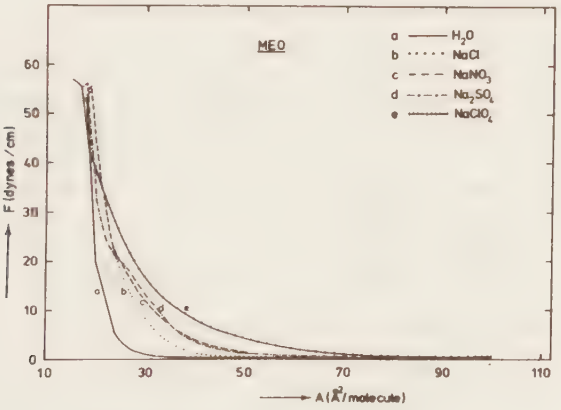


Fig. 32. The F-A isotherms of MEO on various substrates (1m/litre) at 24 °C.

In fig. 32 the effects of different salts in the subphase upon the F-A isotherms of MEO monolayer are shown. Again an expanding

effect of anions on the condensed monolayer of MFO is observed. The $NaClO_4$ caused the largest expansion of the monolayer. Sodium sulphate and nitrate have almost the same expansion effects in the expanded region of the monolayer. However, at the area of 25 $Å^2$ the isotherm on Na_2SO_4 (d) shifts towards lower areas and smaller pressures than the isotherm on other salts and acquires the solid form. The L_c-S transition of curve (d) of Na_2SO_4 is smoothened and in the solid state the monolayer is more condensed than in case of the other anions. Sodium chloride expanded the monolayer of MFO least. In the condensed phase the F-A curve of NaCl (b) is identical with curve the curve of $NaNO_3$ (c). The surface tension corrected F-A isotherms of MFO for Na_2SO_4 are included in fig. 32a. The correction of curves (b) and (d) removed the overlapping of curves (c) and (d). The expansion of isotherms is found in the same serie of anions as for OD.

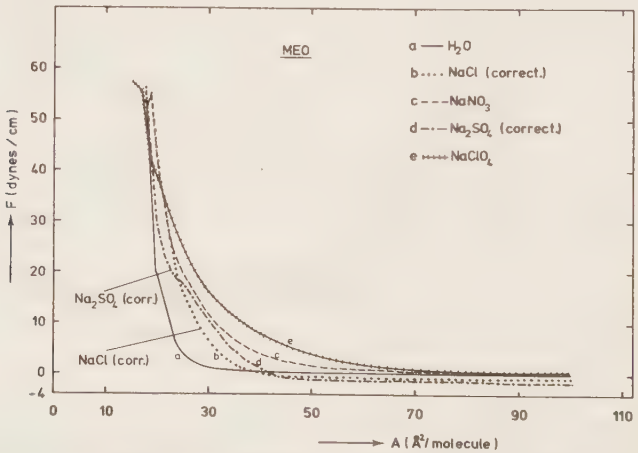


Fig. 32a. The F-A isotherms of MFO on various substrates including the surface tension corrected curves on Na_2SO_4 and NaCl at 24 ^oC.

Table IV. Molecular area (A), surface pressure (F) at different transitions of MFO monolayer on various aqueous solutions (1m) at 24 °C.

sub-strate	A at 5 dyn/cm	F at 30 Å²/mol	L_e-L_c tr.A	L_c-S tr.A	L_e-L_c tr.F	L_c-S tr.F	extrap. L_c·A	extrap. S.A
(1m)	Å²/mol.	dyn/cm	Å²/mol	Å²/mol	dyn/cm	dyn/cm	Å²/mol	Å²/mol
H_2O	24,0	1,2 ± 0,3	24,0	20,0	5,0	20,0 ± 0,4	25,0	21,0
Na_2SO_4	37,4	13,0 ± 0,4	26,0	20,0	19,0	32,0 ± 0,4	-	22,8
NaCl	32,8	8,6 ± 0,4	24,0	20,0	20,8	44,2 ± 0,4	27,0	23,6
$NaNO_3$	36,0	11,6 ± 0,4	24,0	20,0	21,6	45,1 ± 0,4	27,0	23,8
$NaClO_4$	47,5	16,5 ± 0,5	-	18,6	-	43,1 ± 0,2	-	24,0

In table IV some values from the F-A data of MEO for various substrates are summarized, which explain the different properties of MFO monolayers. In the expanded phase $NaClO_4$ has the most dominant effects on the MFO monolayer, as shown by the A values at 5 dynes or the F values at 30 Å² in table IV. The larger area and the higher pressure may be due to the increased and stronger hydration of the hydrophilic group of MFO in presence of $NaClO_4$, since the latter increases the water content of ethylene oxide much more than any other salt studies (15).

4.1.2 F-A isotherms of DFO, TFO and QFO (expanded)

The molecules with the higher number of FO units ($n > 1$) as polar groups showed the expanded form of monolayer isotherms. Such molecules may have a different configuration at

the interfaces at same temperature than their lower homologues. The monolayers of DFO, TFO and OFO are affected by salt addition in a similar way as OD and MFO in the expanded region. The reason might be the increasing intermolecular interaction between polar groups and underlying water with the addition of investigated salts in it. The extent of influence of the various anions may be of a different degree, but the sequence of the anions for all the three monolayers remains almost the same.

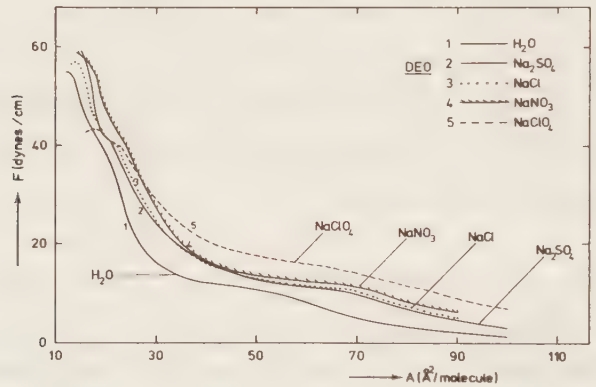


Fig. 33. The F-A curves of DFO on various substrates at 24 °C.

In fig. 33 the F-A curves of DFO are shown on various substrates, the monolayer of DFO expanded with the addition of salts in the subphase. The anions of sulphate, chloride and nitrate show little difference by influencing the F-A curve of DFO, at least when the molecules are at larger distance. However, at smaller distances, where the monolayer supposedly acquires the condensed form, sulphate contributes more to the solidification of the DFO monolayer than chloride and nitrate. All the three anions show a significant

effect by changing the physical properties of DFO monolayer with respect to water. The most dominant effect is observed by $NaClO_4$, the monolayer collapsed before acquiring the condensed part of the curve. The curves of DFO at Na_2SO_4 and NaCl are corrected and shown along with the original curves in fig. 33a.

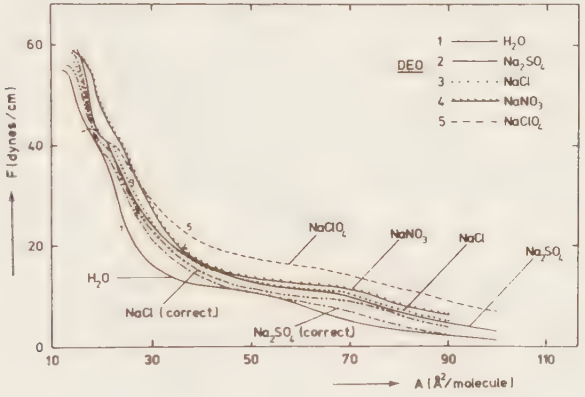


Fig. 33a. The F-A curves of DFO, corrected for surface tensions of Na_2SO_4 and NaCl solutions along with the original curves at 24 °C.

The overlapping of the curves for Na_2SO_4 and NaCl is disappeared and clear effects of anions on DFO monolayer are found in the following order:

$$Na_2SO_4 < NaCl < NaNO_3 < NaClO_4$$

Some physical properties of the DFO monolayer like molecular area, surface pressure at certain points and transitions are summarized in table VI. The first two columns represent the expanded state of the DFO monolayer and the results are found well in agreement with the lyotropic serie of anions. It is interesting to note that L_e-L_c transition for all the salts is almost the same.

Table VI. Molecular area (A), surface pressure (F) of DEO on various substrates at 24 °C.

substrate (1m)	A at 10 dynes/cm $Å^2$/ mol.	F at 70 $Å^2$/ mol. dynes/cm	A at L_e-L_c tr. $Å^2$/mol.	A at L_c-S tr. $Å^2$/ mol.
H_2O	55,0	4,8	5[illegible],0	20,0
Na_2SO_4	68,0	8,9	6[illegible],5	21,8
NaCl	70,0	10,5	7[illegible]	22,0
$NaNO_3$	82,0	11,5	7[illegible]	24,0
$NaClO_4$	86,0	13,7	7[illegible]	23,0

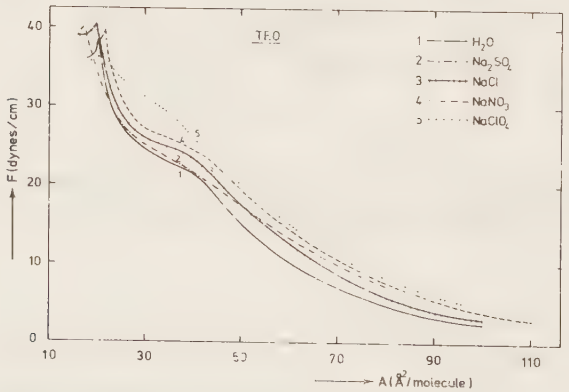


Fig. 34. The F-A curves of TFO on various substrates at 24 °C.

In fig. 34 the F-A isotherms of TFO monolayers are plotted for various sucstrates; similar effects of anions upon monolayer properties are observed as in the case of MFO and DFO. In the F-A curve of TFO there is no L_c-S transition observed, but L_e-L_c transition appeared at 40 $Å^2$ on water.

Sodium chloride and sodium nitrate shifted the L_e-L_c transition slightly towards larger area, i.e., 42 $\mathring{A}^2$, as well as expanded the TFO monolayer to a different degree. The shape of the curve remains the same as for water.

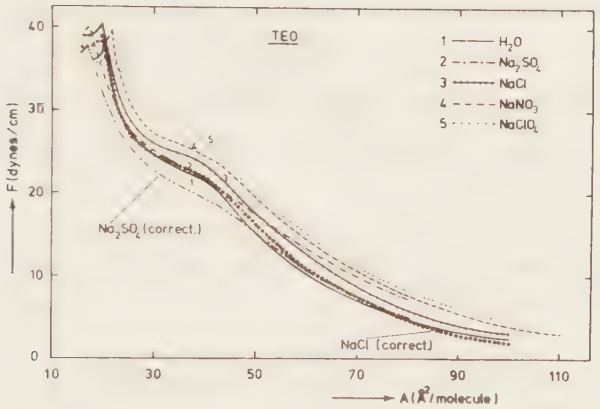


Fig. 34a. The F-A curves of TFO on various substrates at 24 °C, along with surface tension corrected curves of TFO for Na_2SO_4 and NaCl.

Sodium sulphate and sodium perchlorate, on the other hand, show some interesting effects on the transition area of TFO. The L_e-L_c transition shifts towards larger area, 45 $\mathring{A}^2$, and lower pressure in the presence of sulphate, while towards lower area, 36 $\mathring{A}^2$ and higher pressure in the presence of perchlorate. It is worth noting that similar effects have been found by varying the temperature. With the increasing temperature the L_e-L_c transition shifted towards lower area (figs. 13,14) as in case of $NaClO_4$, whereas with decreasing temperature the L_e-L_c transition shifted towards larger area (figs. 13,14) as for Na_2SO_4.

Sodium sulphate shows strange behaviour at larger areas, where the surface pressure values of TFO on Na_2SO_4 are more than on NaCl solution. On correcting the F-A curves to the surface tension values of all the solutions, given in table III, Na_2SO_4 showed instead of expanding effects the condensing effect upon TFO monolayer. This is shown in fig. 43a, where the two corrected curves of Na_2SO_4 along with the original curves are plotted. The order of expansion of the monolayer is then:

$$Na_2SO_4 < NaCl < NaNO_3 < NaClO_4$$

Table VII. Molecular area (A), and surface pressure (F) of TFO on various substrates at 24 °C.

sub-strate (1m)	A at 30 dynes/cm	F at 40 Å² A/ mol.	L_e-L_c tr. A	L_e-L_c tr. F	collapse A
H_2O	23,2	21,8	40,0	21,8	20,5
Na_2SO_4	22,8	22,0	45,0	19,5	17,3
NaCl	24,0	23,5	42,0	22,0	20,0
$NaNO_3$	26,0	24,4	42,0	24,0	21,8
$NaClO_4$	32,5	26,0	36,0	28,0	21,0

The molecular area of TFO at some constant pressure, say 30 dynes per cm (1st column, table VII), is decreased in presence of Na_2SO_4 , but increased by other salts. The perchlorate ions cause an expansion of the area per molecule of TFO by about 10 Å², (col.1st.tab.VII) which is due to the higher degree of hydration caused by the ClO_4 ion. The shifting of the L_e-L_c transition from 40 Å² for water towards larger area (45 Å²) for sulphate and smaller area (36 Å²) for perchlorate is due to the different degree of hydration,

which consequently may influence the configuration of the TEO molecule in a similar way as the variation of temperature (fig.14).

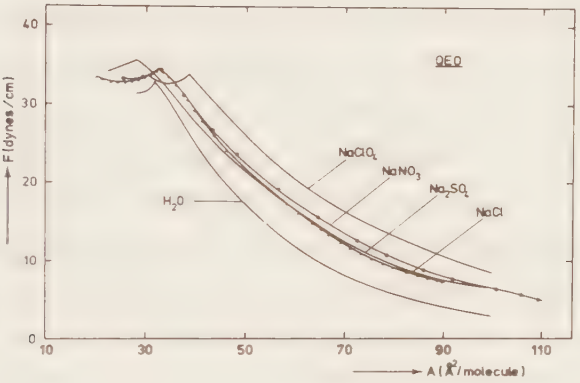


Fig. 35. The F-A curves of QEO on various substrates at 24 °C.

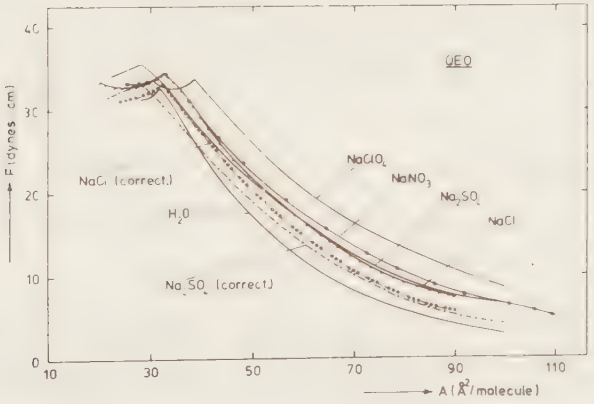


Fig. 35a. The F-A curves of QEO on various substrates at 24 °C with the surface tension corrected curves of Na_2SO_4 and NaCl.

In fig. 35 the F-A curves of QFO on various substrates are shown. The salt addition expanded the monolayer, particularly in presence of $NaClO_4$ the isotherm of QFO is much more affected than in the presence of other salts. The overlapping of QFO F-A isotherms for Na_2SO_4, NaCl and $NaNO_3$ is overcome by the surface tension corrections of the curves for Na_2SO_4 and NaCl in 35a. The hydration of QFO depends upon the nature of the anion. In the presence of $NaClO_4$ the most expanded curve suggests the most hydrated structure of QFO, the area of collapse is found also larger than in the presence of other ions. At larger areas NaCl, Na_2SO_4 and $NaNO_3$ showed somewhat similar results, but in the collapse region sulphate contracts the moleclues to smaller areas, whereas chloride and nitrate increase the area of the molecule a little in comparison to water. The effects of anions have become clearer after the correction of the curves for the surface tension of sulphate and chloride solutions in fig. 35a, the order of expansion of QFO is found in the following way:

$$H_2O < SO_4^{--} < Cl^- < NO_3^- < ClO_4^-$$

4.2 Discussion

There are three components of the surface pressure of a monolayer; the interaction between hydrophobic-hydrophobic chains of the film molecule, the interaction between hydrophilic-hydrophilic groups of film molecules, and the interaction between the molecules of subphase and hydrophilic groups of film molecules. In this chapter only the last typeof interactions are to be considered, since the hydrophobic as well as hydrophilic part of the

film molecules remained the same for the salt studies. By replacing the trough solutions for every monolayer of PEO (e.g. OD, MFO, etc.) the contribution of various anions to the intermolecular interaction between polar group of film molecules and water has quantitatively been determined.

Are the salt effects on the monolayers of PEO observed by F-A measurements comparable to the salt effects determined by other methods? Can the F-A isotherms be considered only a two-dimensional phenomenon? How can the different ions in the subphase influence the monolayers of PEO? In the following sections such questions have been taken into consideration.

4.2.1 Effect of anions and 'structure-temperature' ($T_{str.}$)

The structure of the monolayer and the shape of the F-A isotherm is changed by the addition of salts to the subphase. The salt effect depends upon the ions present in the subphase, sodium perchlorate, for instance, expanded the monolayers of PEO more than sodium sulphate and other salts. For the increase in molecular areas and surface pressures of PEO monolayers upon different substrates the following order is found:

$$Na_2SO_4 < NaCl < NaNO_3 < NaClO_4$$

In the expanded regions of the F-A isotherms the influence of Na_2SO_4 is difficult to understand, since it caused larger F values then NaCl. The elevation of the surface tension of water by Na_2SO_4 seems to be the probable reason for higher values of the surface pressure of the monolayer on it. By correcting the surface tension values for various solutions the overlapping of F-A curves could be overcome and the effects of different salts are

found according to the Hoffmeister [7] series of anions. The effects of anions found by the F-A measurements are in line with the results found by other methods [1,7,19].

Luck [97] confirmed spectroscopically the Hoffmeister series by measuring the 'structure-temperature' (T_{str}) of various electrolyte solutions, and suggested that the Hoffmeister series of ions corresponds to the effects on water structure. Luck used $T_{str.}$ to classify the ions into two groups, the structure-breakers and the structure-makers (see section 2.2).

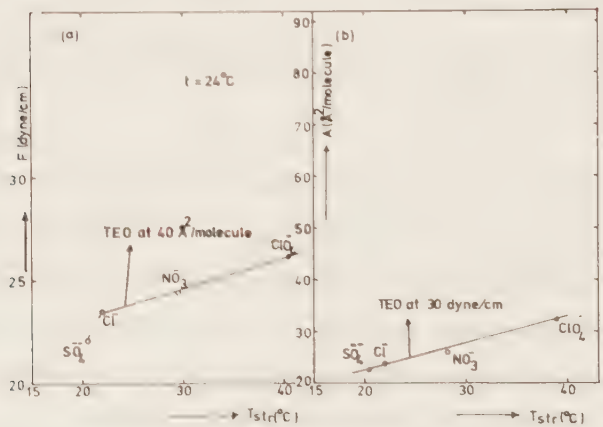


Fig.36. (a) Surface pressure of TEO at A = 40 $Å^2$/molecule as function of $T_{str.}$ of aqueous solutions.
(b) Molecular area of TEO at F = 30 dynes/cm as function of $T_{str.}$

In fig. 36 surface pressure and molecular area of T E O are plotted against $T_{str.}$ of different aqueous solutions at constant area and pressure respectively. The structure temperature of an aqueous solution is equal to that of pure water, when the content of H-bonds in the aqueous solution is equivalent to that in pure water. The surface pressure increased linearly, exept for sulphate, with increasing $T_{str.}$, suggesting the increasing interaction between spread molecules of T E O and water according to the nature of the anions in the subphase. Similarly the molecular area increases linearly at constant pressure for different anions according to $T_{str.}$ (fig. 36). This may suggest the involvement of different degree of hydrogen bonding between the ethylene oxides of T E O and water molecules for different salts in the subphase. The increasing of area per molecule by salt addition is the consequence of increasing hydration of polar groups of film molecules by means of H-bond formation. Thus the anions with higher $T_{str.}$ values, the structure-breakers, hydrate TEO molecules stronger than those with smaller $T_{str.}$ values, the structure-makers.

4.2.2 Energy of dehydration (E_d) of OD and MEO and $T_{str.}$-

The molecules at larger areas possess much freedom and move in random, but under compression they arrange themselves in some certain configuration. The molecules of the spread monolayers get hydrated either when the temperature increases or when salt is added in the substrate. Under the compression of the monolayer the water molecules attached to the polar group would be squeezed out when the monolayer molecules are forced into a

closest-packed arrangement. The hydration of the monolayer depends upon the nature of the ions present in the subphase, as it is evident from table III and IV. This means that the energies on compression of the monolayers for different substrates, would varyif the spread molecules would be compressed from the gaseous or expanded state to the closed-packed solid state. In the solid or close-packed arrangement the molecules of the monolayer are either completely or at least partly dehydrated.

Should the spread molecules retain the same content of hydrated water during compression of the monolayer from expanded to solid state, the monolayer molecules must use an equivalent energy against the energy of compression (F_c). Then this energy would be called " energy of dehydration " (F_d), which can be calculated from the F-A isotherms by equation 22, (see also section 3.2.8 ,page 53).

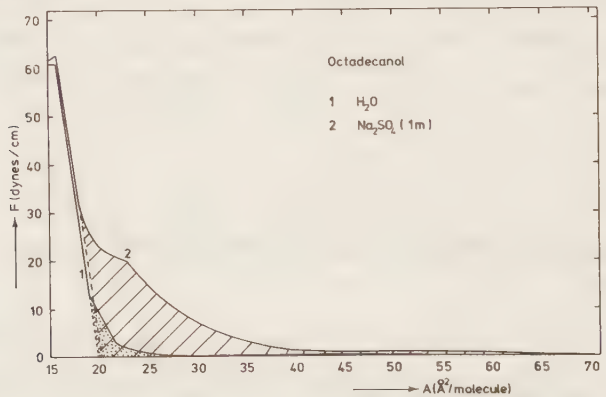


Fig. 37. The integrated areas of the F-A curves of OD; (1) dotted integrated area for water as substrate; (2) lined integrated area for Na_2SO_4 (1m) as substrate at 24 °C.

Certainly F_d includes the contribution from interaction between hydrophilic-hydrophilic groups of film molecules, but the variable factor here is the constitution of the subphase and not the nature of the film molecules. Hence, the E_d calculated for OD or MEO monolayers on different salts is due to the interaction between film molecules and subphase molecules, which is dependent upon the nature of the ions present in the subphase. In fig. 37. the F-A isotherms of octadecanol at water and on Na_2SO_4 (1m) at 24 °C are given, the dotted integrated area of the curve (1) gives the energy of compression (E_c) or energy of dehydration (E_d) for H_2O, whereas the shaded lined area of curve (2) gives F_c or F_d for Na_2SO_4 (see also section 3.2.8). The calculated values of F_d of OD and MEO are reported in table VII.

Table VII. Energy of dehydration (E_d) in erg/mole of OD and MEO on various substrates at 24 °C.

sub-stance	H_2O	Na_2SO_4 (1m)	NaCl (1m)	$NaNO_3$ (1m)	$NaClO_4$ (1m)
OD	$0{,}035 \cdot 10^{10}$ $\pm$ 0,004	$0{,}65\ 10^{10}$ $\pm$ 0,05	$0{,}77 \cdot 10^{10}$ $\pm$ 0,11	$0{,}97 \cdot 10^{10}$ $\pm$ 0,08	$1{,}19 \cdot 10^{10}$ $\pm$ 0,17
MEO	$0{,}118 \cdot 10^{10}$ $\pm$ 0,03	$0{,}76 \cdot 10^{10}$ $\pm$ 0,01	$0{,}84 \cdot 10^{10}$ $\pm$ 0,03	$1{,}20 \cdot 10^{10}$ $\pm$ 0,08	$1{,}62 \cdot 10^{10}$ $\pm$ 0,23

The F_d values of both OD and MEO increase in the lyotropic[7] sequence of anions, i.e.,

$$Na_2SO_4 < NaCl < NaNO_3 < NaClO_4.$$

Sodium sulphate showed a larger expanding effect on the F-A iso-

therms of OD and MFO than sodium chloride, but the molecules of both the monolayers in smaller areas appear to be very closely packed (i.e., dehydrated) in presence of the former. E_d represents the whole integrated area of the F-A curves, which is larger in case of NaCl than for Na_2SO_4, hence the E_d value is larger for the former than for the latter (table VII). It appears from the table V that the polar groups of OD and MFO are much more hydrated in presence of $NaClO_4$ than in presence of Na_2SO_4 and other salts. Similarly more E_d is needed for the monolayers at higher temperature than those at lower temperature (see table III). The E_d values of MFO can also be compared to the water content per ethylene oxide unit of $H_{17}C_8$-C$_6$H$_4$-$(OCH_2CH_2)_9$-OH (PIOP-9) in the presence of ions at 80 °C, calculated by Luck [15]. The energy of dehydration of OD and MFO are found in line with the 'structural temperature' of various aqueous solutions determined spectroscopically [97]. Fig. 38 shows the energy of dehydration

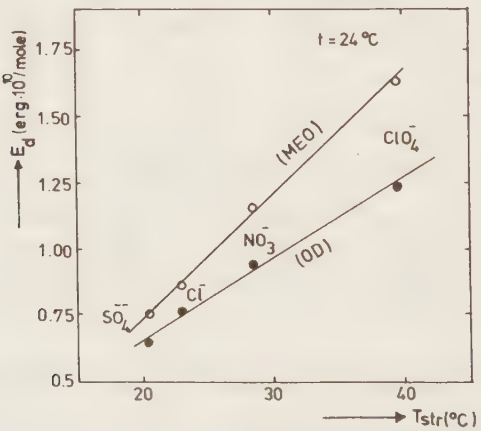


Fig. 38. "Energy of dehydration" (E_d) of OD and MFO against $T_{str.}$ of aqueous solutions at 20 °C.

of OD and MFO plotted against $T_{str.}$ at 20 ^{o}C for various aqueous solutions. Within the experimental error F_d is found in good agreement with $T_{str.}$, which is a direct measure of hydrogen bond content of aqueous solutions. The more the $T_{str.}$ is, the more free -OH groups in the solution would be present. Hence, the higher values of F_d for ClO_4^-, for example, is due to stronger interaction between water molecules and spread molecules in the form of hydrogen-bond formation, which means stronger hydration of OD and MFO in presence of $NaClO_4^-$ than the other salts studied.

4.2.3 F-A isotherms, a `two-dimensional' phenomenon ?

The large interactions between hydrophilic groups of PEO and water, either due to increasing number of EO units or with increasing temperature or by addition of salts, are an indication that the F-A isotherms are not only two-dimensional phenomena. The polyethylene oxides form hydrogen-bonds with water, which is always a three-dimensional phenomenon. The effects of salts found on the monolayers of PEO at the air-water interface are parallel to the effects of salts on polyethylene oxides in bulk, where the hydrogen-bond formation plays a dominant role[26,76]. Hence the F-A isotherms could not merely be considered a two-dimensional phenomenon. As the content of water of the hydrophilic group of PEO increases by means of salts or temperature, the increased hydration of polar groups may change the configuration of the PEO molecules. Thus, it is quite possible that the molecules of PEO may partly be pulled into or out of the interface, depending upon the interaction with the underlying subphase.

Some similar considerations have been made by Heusch [64] and Becher [69] for the ethylene oxide derivatives at the air-water interface. From the results so far obtained from the HHB or temperature or the salt effect investigation of PEO monolayers, one can conclude that the F-A isotherm may be considered a three-dimensional phenomenon, particularly when the interactions between polar group and underlying subphase are under consideration (see also page 18).

4.2.4 Hydration of PEO monolayers under ionic influence

How can the ions present in the subphase influence the F-A isotherms of the monolayers?

There may be different views about the ways the ions in the subphase can influence the monolayers. The author thinks an indirect effect of ions on monolayers rather than any direct interaction with the latter more appropriate, for the following reasons.

The polyoxyethylene derivatives are non-ionic in nature and most suitable for the direct interaction with water, in the form of hydrogen-bond formation. The rise in temperature and the addition of salts change the structure of water by varying the content of non hydrogen-bonded OH-groups [1]. Thus these free OH groups may form the hydrogen bonds with the oxygen atom of EO and hydrate the hydrophilic group of the spread molecules. Hence the hydrated monolayers in the presence of salts show larger molecular area and the higher surface pressure in comparison to those on water. Different ions change the water structure to a different extent, perchlorate, for example, has the largest effect in comparison to other salts used in this investigation.

Specific ionic effects are related to the size of the hydrated ion,

namely, a decrease in the lyotropic number corresponds to the decrease in hydrated ionic radius [68]. The overall solubility or micelle formation of the non-ionic detergents depend upon the extent of hydration of the hydrophilic portion through the formation of hydrogen bonds between the ether oxygen and water molecules [26]. The solubility or the hydration of the EO group in bulk is for various anions found to agree with the Hoffmeister ion series [26, 76]. This is parallel to our results from the F-A isotherms of PEO.

The ions known as structure-breakers, eg. ClO_4, have salting-in effects, while the structure-makers, eg. SO_4, have salting-out effect upon the ethylene oxides [15]. The salting-in effects of the ions on the monolayers of PEO may be considered as due to the increased hydration of the PEO mplecule, whereas the salting-out effect by ions could be ascribed to diminished hydration of the spread molecules.

The extent of dehydration of PEO is found in the lyotropic series of anions, shown above. The energy of dehydration (E_d) of OD and MEO, calculated from the F-A curves of both, could support the view of hydration. Energy of dehydration of OD and MEO increases with the increasing structure temperature of different salt solutions found according to Hoffmeister series of ions. Thus more E_d would be needed to force the monolayer molecules in their close-packed arrangement from expanded phase for $NaClO_4$ than for $NaNO_3$ or NaCl or Na_2SO_4 (see table VII). The elavation of temperature expands the monolayers of PEO, higher energies of compression are observed for PEO monolayers for higher temperatures (see table II). This is connected with a stronger hydration of PEO at higher temperature. Thus the salts having structure-breaking effects influence the PEO monolayers

in the similar way as increasing of temperature i.e. by hydrating the spread molecules. It would be here worth mentioning that the counter-ion interaction between the monolayers and ions in the subphase is usually considered in the case of ionic monolayers[4,54]. This is not applicable to the case of PEO monolayers, which are non-ionic.

4.3 Monolayers of PEO on aqueous solutions of different $NaClO_4$ concentration

Sodium perchlorate had the strongest effect on the monolayers of PEO giving the highest pressure and largest area per molecule of PEO in comparison to any other salt studied. It resembled to the effects of increasing the temperature, at least qualitatively. A study of the dependence of the F-A isotherms of PEO on the different concentration of $NaClO_4$ is very interesting because the latter is known to have particular effects on the structure of water (i.e. structure-breaking effect)[13] and the " salting-in " effect upon the ethylene oxide adducts in bulk [15]. The IR spectrum is influenced largely with increasing concentration of $NaClO_4$, which is shown in fig. 4. Can the effects of the $NaClO_4$ concentration on PEO monolayers be correlated with the effects of $NaClO_4$ on bulk water?

4.3.1 Measurements of F-A isotherms of PEO on $NaClO_4$

A circular teflon trough (CTT) is used to measure the F-A isotherms of PEO monolayers on solutions of $NaClO_4$ of different concentration (0,1m-4m). The trough was thermostated

to 24.5 °C for every measurement. The results are not exactly quantitatively in agreement with those found by the rectangular metalic trough (RMT). There could be many reasons for this discrepancy of results by both troughs, which will be discussed in the experimental part. Nevertheless, the effects of $NaClO_4$ concentration upon PFO monolayers are well elaborated and obvious by these measurements. All the measurements of PFO monolayers for concentration effects are performed with one apparatus, i.e., CTT. The cause of absolute error has not been explored, because the reproducibility was good.

F-A isotherms of MFO

Fig. 39 shows the F-A curves of MFO upon the aqueous $NaClO_4$ solutions of various concentration. The most affected part

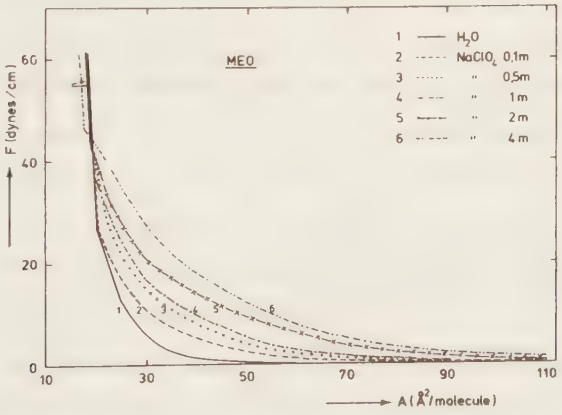


Fig. 39 The F-A isotherms of MFO on aqueous solutions of $NaClO_4$ at 24 °C.

of the curve by increasing concentration of $NaClO_4$ is the liquid between 20 Å^2 and 110 Å^2 molecular areas. The monolayer of MFO on destilled water gave a F-A curve (curve 1) with well defined solid part, a liquid-condensed and an expanded part. With the increasing concentration of $NaClO_4$ the curve expands towards larger area and higher pressure, the L_e-L_c transition at 25 Å^2 for water diminishes and only solid and expanded phases remain present. The liquid-solid transition area remains almost the same i.e. 20 Å^2, but for curve 6 of 4m concentration it is found 18 Å^2. The L_c-S transition pressure increases with increasing concentration. The extrapolated solid area is found for all the concentrations the same i.e. 21.5 ± 0.5 Å^2.

F-A isotherms of DFO

Fig. 40 includes the F-A curves of DFO on different concentrations of $NaClO_4$ solution. The expansion of the DEO monolayer is observed with increasing concentration of $NaClO_4$. Upon the distilled water the F-A curve (1) shows the liquid-expanded (L_e) and liquid-condensed (L_c) phases with L_e-L_c transition at about 55 Å^2. In the same curve (1) a break appears at 19 Å^2 and an undifined region starts till the curve shows a small solid part in smaller areas. A similar behaviour is found for 0.1m concentratio, however, the curve is more expanded than that on water. The L_e-L_c transition is found ~ 55 Å^2 for 0.1m and 0.5m as for water. With the increasing concentration the L_e-L_c transition shifts to about 60 Å^2, but becomes unsharp. In the condensed phase the solid part, which is reproduceable on water, disappears for higher concentrations, exept for 0.1m, which appears at smaller A than

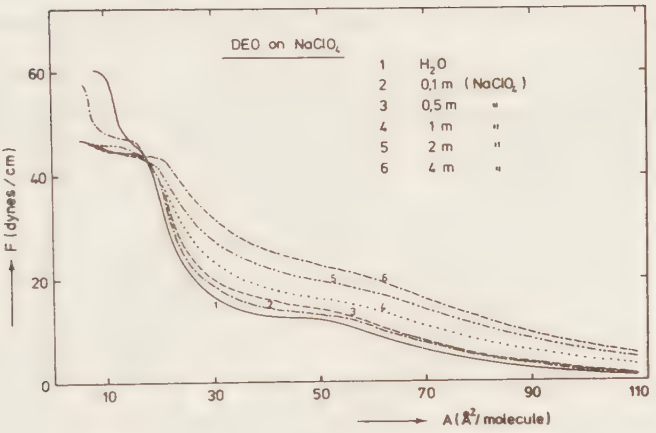


Fig. 40. The F-A isotherms of DEO on aqueous solutions of $NaClO_4$ at 24.5 °C.

20 Å^2. The transition point between solid and liquid phase at 19 Å^2 for water becomes the collapse point for the higher concentration.

F-A isotherms of TEO

The F-A curve of TEO on distilled water is a two-phase diagram, which shows the L_e-L_c transition at 40 Å^2 and collapse point at 21 Å^2 (curve 1, fig. 41). With the increasing concentration of $NaClO_4$ the L_e-L_c transition shifts towards larger areas and for the highest concentration of 2m and 4m this transition disappears. The collapse area shifts also to larger areas, indicating the stronger hydration of TEO molecules with increasing concentration. The disappearance of the L_e-L_c transition in the

curves 5 and 6 in fig. [41] on the concentrated solutions of (2m,4m) $NaClO_4$ resembles to the effect found by the rise in temperature of about 10 °C (compare to fig. 14). Such a transitionless one-phase diagram resembles to that of its higher homologue PEO at room temperature.

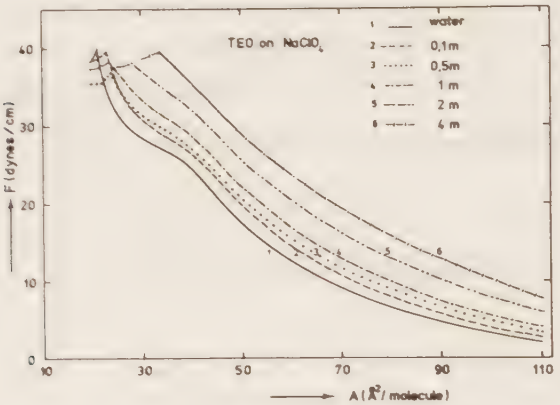


Fig. 41. The F-A curves of TEO on $NaClO_4$ solutions of different concentration at 24.5 °C.

4.3.2 The hydration and intermolecular interaction of PEO molecules in presence of $NaClO_4$.

With the increasing concentration of $NaClO_4$ in the trough solution, the area per molecule of PEO at some constant pressure increases, as shown by figs. 39, 40 and 41. In table VIII the effect of $NaClO_4$ concentration has quantitatively been shown by producing A/A_o values of various monolayers of PEO for different concentrations (A is the area per molecule and A_o the area per molecule at C = 0). It is interesting to note that

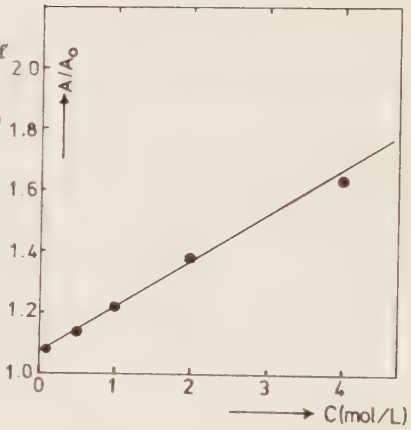
Table VIII. The A/A_o (A is area per molecule, A_o the area per molecule at C=O) values of PEO on $NaClO_4$ solutions (0.1m - 4m).

A/A_o / C (moles/l)	CD	MEO	DEO	TEO	QEO	NEO	average
	A_o=20	A_o=22.4	A_o=26.3	A_o=46	A_o=55.8	A_o=82.8	
at 20 dynes/cm							
0.1	1.15	1.05	1.08	1.08	1.03	1.10	1.08±0.04
0.5	1.22	1.16	1.14	1.12	1.06	1.13	1.14±0.05
1.0	1.29	1.23	1.34	1.17	1.14	1.21	1.22±0.08
2.0	1.38	1.38	1.83	1.33	1.18	1.30	1.39±0.23
4.0	1.58	1.65	2.26	1.48	1.40	1.46	1.64±0.33
	A_o=23	A_o=26.4	A_o=58	A_o=67	A_o=80	-	average
at 10 dynes/cm							
0.1	1.31	1.18	1.07	1.08	1.05	-	1.14±0.11
0.5	1.44	1.38	1.08	1.13	1.13	-	1.23±0.16
1.0	1.58	1.52	1.25	1.20	1.18	-	1.35±0.19
2.0	1.72	1.82	1.43	1.34	1.23	-	1.51±0.25
4.0	1.83	2.06	1.52	1.49	1.43	-	1.67±0.27

irrespective of film substance the ratio A/A_o remains more or less constant for every concentration. However, the deviation of this value for the higher concentrations (2m, 4m) is larger, but for the other three concentrations (0.1m, 0.5m and 1m) it is quite reasonable. The A/A_o values of PEO at 20 dynes/cm are plotted as function of $NaClO_4$ concentration in fig. 42 , which shows a linear increase in area with increasing concentration.

The increase in molecular area establishes the increasing hydration of the PEO molecules with increasing concentration of $NaClO_4$. Since the content of free OH groups in water increases with increasing concentration of $NaClO_4$ (i.e., structure-breaking effect), the chances of hydration of the polar groups of PEO increase in the concentrated solutions of $NaClO_4$.

Fig. 42. The A/A_o values (average) of PEO monolayers (n= 0,1..4 and 9) at 20 dynes/cm (from table VIII) plotted against C (moles/L) of $NaClO_4$ at 24.5 °C.



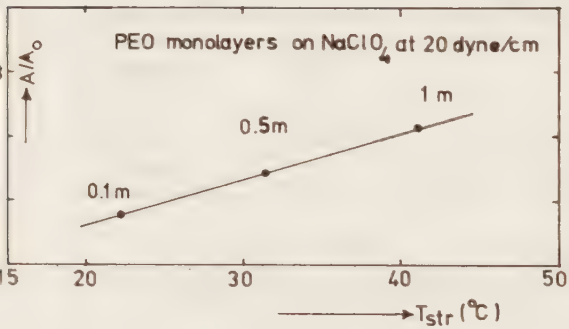
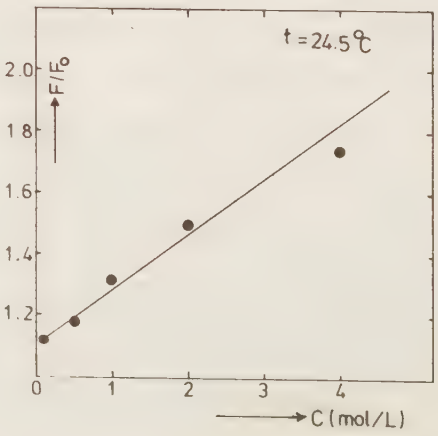


Fig. 43. The A/A_o values (av.) of PEO at 20 dynes/cm plotted as function of T_{str} of 0.1m, 0.5m and 1m solutions of $NaClO_4$ at 20 °C.

Fig. 44. The F/F_o values (av.) of PEO (n > 1) at 60 Å²/mol. (from table IX) plotted against C (moles/L) of $NaClO_4$ at 24.5 °C.



The ratio A/A_o increases linearly, when plotted against spectroscopically determined $T_{str.}$[26] of $NaClO_4$ solutions (0.1m, 0.5m and 1m) at 20 °C, as seen in fig. 43. Increasing of $T_{str.}$ with increasing $NaClO_4$ concentration means the increasing of free-OH groups in water. Thus the agreement between A/A_o and $T_{str.}$ in fig. 43 confirms our view of increasing hydration of PEO molecules with increasing $NaClO_4$ concentration.

Sodium perchlorate shows a sort of 'salting-in' effect upon the PEO molecules, when the latter get strongly hydrated in presence of higher concentration of $NaClO_4$.[1] The hydration of the polar groups of PEO also seems to be responsible for the disappearance of L_e-L_c transitions of DEO and TEO monolayers at higher concentration of $NaClO_4$, as well as for weakening and disappearance of solid states of MEO and DEO, respectively (see figs. 39, 40, 41). For instance, the F-A isotherm of TEO on 2m and 4m concentration solution of $NaClO_4$ resembled to that of QEO on water, a transitionless one-phase isotherm (compare fig. 41 to fig. 11). The increasing hydration with increasing concentration of $NaClO_4$ could influence the configuration of the PEO molecules as the increasing temperature (see section 3.2.5).

The hydration of polar groups of PEO molecules takes place through the formation of hydrogen bonds between the ether oxygens and water molecules.[1] The increase in hydrogen bond formation with salt addition leads to the increased intermolecular interaction between polar groups of PEO and subphase molecules. As consequence the monolayers of PEO show higher surface pressure on higher concentration of $NaClO_4$ (see figs. 39, 40, 41). In table IX the F/F_o values (F is the surface pressure and F_o the surface pressure at C = 0) of PEO at different molecular areas are

reported. Unlike A/A_o values in table VIII the F/F_o values are not constant for all the PEO members, though for expanded monolayers

Table IX. The F/F_o (F is the surface pressure in dynes/cm; F_o is the surface pressure at C = 0) values of PEO monolayers on $NaClO_4$ solutions (0.1m - 4m) at 24.5 °C.

F/F_o / moles/l	DP	MEP	PEP	TEP	HEP	NEP	average
	F_o=0.1	F_o=0.7	F_o= 9	F_o=10.5	F_o=17.7	F_o=31	(n > 1)
at 60 Å² molecule							
0.1	11.0	5.25	1.18	1.16	1.06	1.02	1.13±0.06
0.5	16.1	10.75	1.2	1.29	1.11	1.11	1.18±0.09
1.0	25.3	14.4	1.36	1.36	1.22	1.14	1.30±0.18
2.0	28.1	32.2	1.81	1.62	1.28	1.18	1.50±0.33
4.0	32.5	39.4	2.28	1.88	1.5	1.27	1.74±0.41
at 40 Å² molecule							
	F_o=0.4	F_o=1.2	F_o=13	F_o=24.5	–	–	(n > 1)
0.1	11.25	4.5	1.12	1.04			1.08±0.06
0.5	16.5	6.67	1.23	1.07			1.15±0.11
1.0	21.0	8.33	1.45	1.19	collapsed		1.32±0.18
2.0	25.0	13.33	1.71	1.32			1.52±0.28
4.0	30.0	19.0	2.0	1.45			1.73±0.39
at 30 Å² molecule							
	F_o=1.0	F_o=5.0	F_o=1.65	F_o=28.8	–	–	(n > 1)
0.1	6.5	1.96	1.12	1.07			1.09±0.03
0.5	7.75	2.68	1.18	1.09			1.14±0.07
1.0	9.36	3.96	1.38	1.16	collapsed		1.27±0.16
2.0	10.94	5.64	1.64	1.29			1.47±0.25
4.0	13.36	8.88	1.88	1.34			1.61±0.38

of PFO ($n>1$) the F/F_o values can roughly be considered constant for each concentration. The table IX shows further, that the effect of $NaClO_4$ on the condensed monolayers ($n<2$) is much larger than on the expanded monolayers of PFO ($n>1$), for instance at 40 $Å^2$ per molecule the F of OD monolayer on 4m $NaClO_4$ solution is 30 times more than on water, or the F of MFO on 4m solution is 15 times more than on water. On the other hand, the F of DFO and TFO at 40 $Å^2$ on 4m solution increases only 2 and 1.5 times, respectively, than that on water. The F/F_o values of PFO increase also as a linear function of the concentration of $NaClO_4$, as shown in fig. 44.

It is obvious that the increasing intermolecular interactions between polar groups and subphase molecules with increasing concentration of $NaClO_4$ are responsible for the expansion of the monolayers of PFO. Such intermolecular interactions may be regarded as " repulsive" or "expansive" forces against the "cohesive" forces of the hydrocarbon chains, which contract the monolayers towards lower surface pressures. As the hydration or the water content of polar groups (EO) increases with increasing concentration of $NaClO_4$, more energy of compression would be needed to compress the molecules of PFO monolayers in their close-packed forms. In other words more energy would be used to dehydrate the more strongly hydrated molecules of PFO on higher concentrations than on lower concentrations or water, which is observable in form of increasing surface pressure.

4.4 The surface potential of PFO monolayers on aqueous solutions

For a comparative study of effects of different anions on the surface potential (ΔV) of PFO monolayers, two cases, a condensed monolayer of OD, and an expanded monolayer of TFO, have been selected. Thus the variation in ΔV values observed due to

various anions is mainly the contribution of the reorientation of water dipoles (μ_z), as described by equation 23. The ΔV-A measurements on different aqueous solutions of 0.1m concentration have been done with a vibrationg plate electrode under similar experimental conditions.

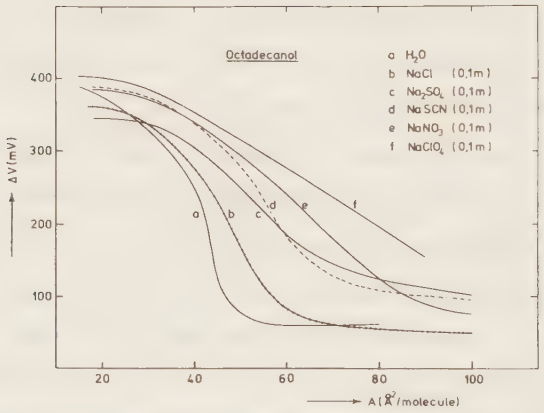


Fig. 45. The ΔV-A curves of octadecanol (OD) at 25 C^{o} on various substrates.

4.4.1 ΔV-A curves of OD

In fig. 45 the surface potential (ΔV) of the OD monolayer is plotted against the molecular area on various substrates. Octadecanol gives a condensed type of F-A curve (see fig. 11) with three distinguishable phases. The addition of anions expanded the F-A curve of OD and the phases of the monolayer were no more well distinguishable. The heterogeneity or the multiphase nature of OD

monolayers's isotherm is evident from curve (a) of fig. 45. The presence of anions diminishes the distinction of such phases and the surface potential of OD increases homogeneously. The increase in ΔV with the compression of the film may indicate the increasing orientation of dipoles , as the molecules of OD as well as the subphase molecules reorient themselves. In table X the values of the surface potential and the dipole moments of OD monolayer for two molecular areas are given, where A = 60 $\mathring{A}^2$ represents the expanded state of monolayer and 20 $\mathring{A}^2$ the condensed solid state. In the expanded state of the monolayer the anions did not follow the Hoffmeister series, particularly the sulphate. In the condensed state (20 $\mathring{A}^2$), however, the ΔV values are in line with the Hoffmeister series of anions. Fig. 46 shows the calculated dipole

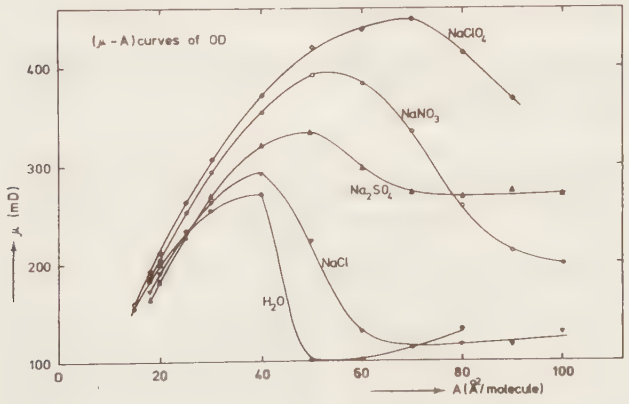


Fig. 46. The μ-A curves of OD for various substrates, calculated from the ΔV-A curves at 25 °C.

moments (μ) plotted against the molecular area of OD, in which the maxima of μ-A curves shift towards larger areas for different substrates in the following order,

$$H_2O \approx NaCl < Na_2SO_4 < NaNO_3 < NaClO_4.$$

On compression of the monolayer the dipole moments of OD for various substrates increase first to their maximum and then decrease, as the monolayer molecules approach near each other. The μ -A curves of OD on various substrates show two parts, a μ-increasing part and second μ-decreasing part. The maxima of the curves shift towards larger areas according to the following salts i.e.,

$$NaCl < Na_2SO_4 \quad NaNO_3 < NaClO_4.$$

The decrease in the μ values in the condensed state i.e. smaller areas might be assumed due to the fact that a gradual orientation of the molecules causes a decrease in the free energy of the surface, which in turn would cause a decrease in the surface dipole moment[78]. Schulman and Hughes[54] reported such maximums for fatty acids μ-A curves.

Table X. Surface potential (ΔV) and dipole moment (μ) of octadecanol on various substrates at 25 °C.

substrate 0.1 m	60 Å²/molecule		20 Å²/molecule	
	ΔV (mV)	μ (mD)	ΔV(mV)	μ (mD)
H_2O	63 ± 11	100	375 ± 8	199
Na_2SO_4	187 ± 18	298	343 ± 7	182
NaCl	82 ± 1	131	361 ± 4	192
$NaNO_3$	241 ± 23	384	386 ± 13	205
NaSCN	183 ± 17	291	388 ± 1	206
$NaClO_4$	275 ± 7	438	400 ± 3	212

4.4.2 ΔV-A curve of TFO

The reverse order of anions for the increase in ΔV values of TFO monolayer is found compared to the monolayer of OD.

Fig. 47 shows the ΔV-A curves of TFO monolayer at various substrates, for the sake of clarity the curve for $NaNO_3$ is omitted, which resembles to that of Na_2SO_4. According to these effects the anions can be classified into two groups: one comprising of ClO_4 and SCN anions with ΔV values less than for water, and the second group showing

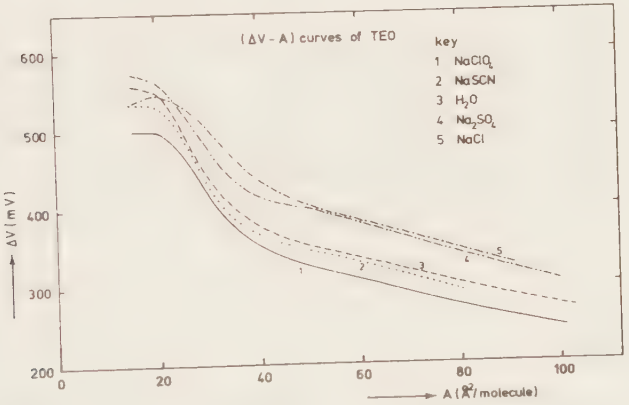


Fig. 47. The ΔV-A curves of TFO on various substrates of 0.1 molar concentration at 25 °C.

higher values than water i.e. Cl^-, NO_3^- and SO_4^{--}. Such classification of salts is known from the turbidity points (T_k) measurements of the aqueous solution of PIOP-9, where the T_k values of $NaClO_4$ and NaSCN are higher than T_k without salt addition (i.e. 64 °C), and for NaCl, $NaNO_3$ and Na_2SO_4 the T_k values are less than 64 °C (1). Table VI shows the ΔV values and μ, calculated from the ΔV-A curves, of TFO at 40 Å^2 and 25 Å^2. The compression of the monolayer reduces the dipole moment of the molecule, but increases the surface potential of the monolayer.

Table VI. Surface potential (ΔV), surface dipole moments (μ) of TFO on various substrates at 25 °C.

substrate	at 40 Å^2		at 25 Å^2	
0.1m	ΔV (mV)	μ (mD)	ΔV(mV)	μ (mD)
H_2O	376	399	503	334
Na_2SO_4	415	432	525	348
NaCl	417	442	520	348
$NaNO_3$	413	438	530	352
NaSCN	370	393	495	328
$NaClO_4$	354	376	473	314

4.4.3 Discussion

Jarvis and Scheiman [79] measured the surface potentials of various electrolyte solutions (without any monolayer on the surface) by the ionizing electrode method and found the increase in ΔV in the following order,

$$SO_4^{--} > CO_3^{--} > Cl^- > NO_3^- > SCN^-.$$

However, at the low concentration, say 0.1m, the difference in ΔV was negligibly small i.e., within ± 5mV. They supposed the effects of ions upon the surface potential related in some manner to the structure of water molecules in the ionic co-sphere, as influenced by ionic charge and ionic radius. At the interface the ions may not be uniformly distributed, and it is obvious that the forces operating on a molecule will ba unsymmetrical. Weyl [80], Fletcher [81] have argued that the water molecules at the air-water interface have a preferential orientation, with the oxygen atom outermost. According to Jarvis and Scheiman such orientation

would establish a double layer with positive portion directed into the solution, one might expect a preferential accumulation of the anions near the interface. Such an arrangement of water surface would be changed when a monolayer is spread on it. The water molecules reorient around the hydrophilic group of the monolayer and the measured surface potential is then a combination of various components, as mentioned earlier.

The results so far obtained by the author for the nonionic monolayers of PEO and by Blaisance and Ter-Minassian-Saraga [77] for the ionic monolayer of polysoaps suggest that the anions present in the subphase contribute significantly to the surface potentials of the monolayers, as expected from equation 23. The ionic effects on ΔV of ionic monolayers could be considered in the terms of counter-ion interactions of ions with the monolayers [77]. In case of nonionic PEO monolayers it can be assumed that the variation in ΔV is due to the different extent of reorientation of water molecules around the polar groups of film molecules in presence of different anions. Jarvis and Scheiman [79] pointed out that the molecular structure of water in association with the ions in the study of surface potential cannot be ignored.

4.5 The effect of pH and sodium phosphates on PEO monolayers

It is rather difficult to separate the influence of the pH from the salt effects, since the presence of inorganic or organic ions influences the monolayer as well. To solve the problem, however, systematic measurements of the PEO monolayers on 0.1m sodium-phosphate, -monohydrogenphosphate and-dihydrogenphosphate solutions, having 13.1, 9.8, and 5.1 pH values respectively, were carried out. All measurements have been performed on a 0.1m solution

in the trough. The circular teflon trough has been used. To measure the surface potentials and the surface pressure, the vibrating plate electrode and the Wilhelmy balance respectively have been used, while the temperature has been kept constant for all the measurements.

4.5.1 F-A isotherms of DFO

At higher areas there is no remarkable difference between the three F-A curves of DFO for various phosphate ions, but in comparison to the pure water as subphase the pressure is higher (fig. 48). The following order of expansion of the monolayer between 70 Å^2 and 19 Å^2 is found for various substrates,

$$H_2O < NaH_2PO_4 < Na_2HPO_4 < Na_3PO_4.$$

The transition area at 55 Å^2 shifts towards a larger area on adding the phosphate solutions to the substrate. Similarly the break at 19 Å^2 in the F-A curve of water shifts to 22 Å^2 in case of Na_3PO_4. As at A = 19 Å^2 the film is rather unstable, it is difficult to find the exact limiting area of the molecule.

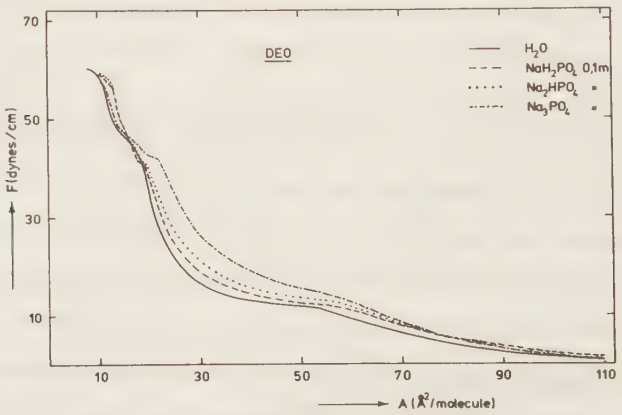


Fig. 48. The F-A curves of DFO on various substrates at 24.5 °C.

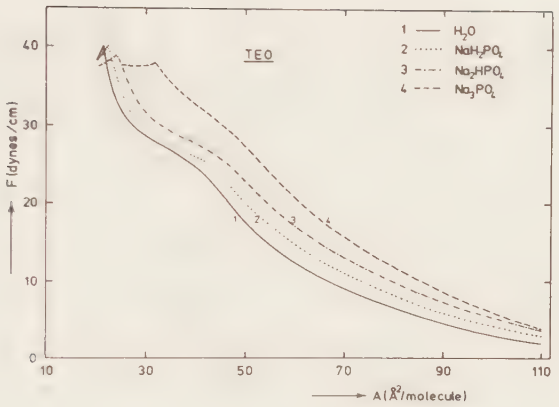


Fig. 49. The F-A curves of TFO on distilled water and 0.1m solution of sodium mono-, di-, and tribasic phosphates at 24.5 °C.

The expansion of the monolayer of TFO is very clear in fig. (49), when the phosphates are added in the substrate. The order of expansion of the TFO monolayer is found the same as for the DFO monolayer. The transition area at 40 $Å^2$ in curve (1) shifts to 43 $Å^2$ in curve (2) and to 46 $Å^2$ in curve (3), whereas in curve (4) for Na_3PO_4 it almost disappears. The collapse point increases from 21 $Å^2$ for water to 22.5 $Å^2$ for NaH_2PO_4, to 24 $Å^2$ for Na_2HPO_4 and to 32 $Å^2$ for Na_3PO_4.

4.5.2 Monolayers of PFO and phosphate solutions

The effects found on the F-A isotherms are considered due to the phosphate (monobasic, dibasic, tribasic) ions in the solution. Such effects are reported in the figures (48) and (49), showing more expansion of the monolayer by tribasic phosphate than by dibasic, monobasic-phosphate and in the absence of phosphate. The increase in pressure at various molecular areas of the PFO monolayers by mono-, di-, and tribasic phosphate anions has

further been summarized in the figures (50). in the expanded states i.e., at larger areas, all the three phosphates have not shown

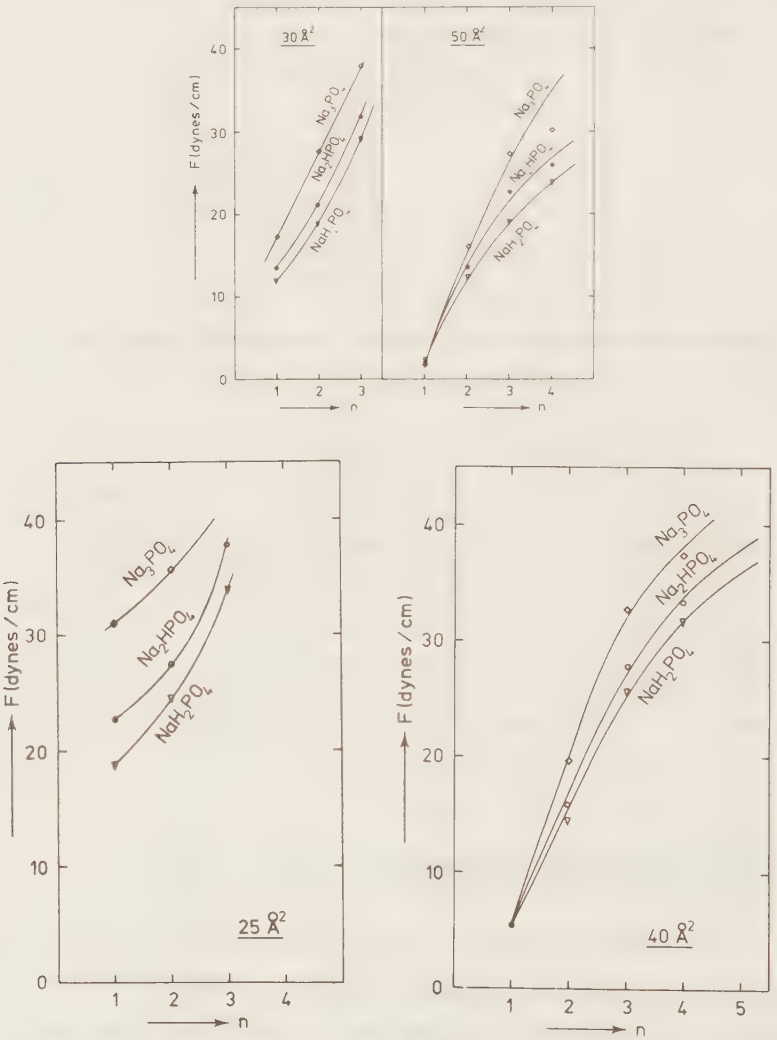


Fig. 50. The surface pressure (F) of PEO monolayers plotted against the number of EO units (n) for the substrates of sodium phosphate, sodium monohydrogen phosphate and sod. dihydrogen phosphate at certain molecular areas representing the expanded and condensed state at 24.5 °C.

any effect on MFO (n= 1), while for higher numbers of EO groups the pressure increases in the following order:

$$H_2PO_4^- < HPO_4^{--} < PO_4^{---}.$$

In the condensed state the three phosphates show a significant increase in pressure for lower members of PEO also. The shifting of the transition points towards higher areas due to the phosphate solutions are in a line with the previous results of other salts. The increase in molecular area at some constant pressure is in the same order as the surface pressure. This means the molecules get more hydrated in the presence of a sodium phosphate solution than in the presence of a sodium dihydrogen phosphate solution. This suggests that the polar groups are interacting with a larger number of water molecules when the sodium phosphate is in the solution, causing a higher force in the F-A isotherm. This behaviour of phosphate seems reverse to the interaction between mono-, di-, and tribasic phosphate molecules and water molecules. It is generally believed that Na_3PO_4 has a more associating tendency for water than Na_2HPO_4 and $NaHPO_4$. In table VII it is shown that Na_3PO_4 solution has higher water content than NaH_2PO_4 and that monobasic phosphate displaces more water than di- and tribasic solutions.

Table VII: Molar concentration (M), anhydrous solute concentration (C_s), total water concentration (C_w), and water displaced by anhydrous solute (C_o-C_w) of mono-, di-, and tribasic phosphate at 20 °C(82).

substance	M g.mol/l	C_s g/l	C_w g/l	(C_o-C_w) g/l
NaH_2PO_4	0.126	15.1	994.2	4.0
Na_2HPO_4	0.107	15.2	997.9	0.3
Na_3PO_4	0.125	20.4	1001.2	-2.9

Could the concept of hydration be applied, then more hydrated PEO structure should have been obtained in the presence of monobasic phosphate. But the strange reverse behaviour seems to have its roots somewhere else. The different concentrations ofcations at the same concentration of solution may have affected the results, which remains to be proved.

Could the condensation of the monolayer by ions be considered a direct interaction with the monolayer, then it seems probable that there could be some sort of direct link between monobasic phosphate and the monolayer. Then it could be assumed that two hydrogen atoms of NaH_2PO_4 may probably form some hydrogen bonds with the oxygen atom of the ether groups of the monolayer, whereas Na_3PO_4 does not have such a possibility. This sort of interaction may contract the monolayer inspite of a higher water content, displaced by NaH_2PO_4, available to the polar group for hydration.

4.5.3 ΔV-A measurements

Fig. (51) shows that sodium-dihydrogenphosphate (pH = 5.1) in the subphase gives the highest surface potential values for the OD monolayer at every molecular area (curve 4). On the other hand the OD monolayer on distilled water gives the minimum surface potential values (between 65 Å^2 and 35 Å^2), although the pH value of water (pH = 5.5) is not very different from that of the dihydrogenphosphate solution. This fact casts some light upon the difference between the influence of salt and the hydrogen ion concentration on the monolayer properties. Sodium hydogen phosphate (pH = 9.9) gives the second highest values of ΔV (curve 3), whereas sodium phosphate (pH = 13.1) according to curve (2) gives smaller values than for mono-, and diphosphate solution and moreover,

the ΔV values on the phosphate solution at areas larger than 70 $Å^2$ or smaller than 30 $Å^2$ are even lower than on water.

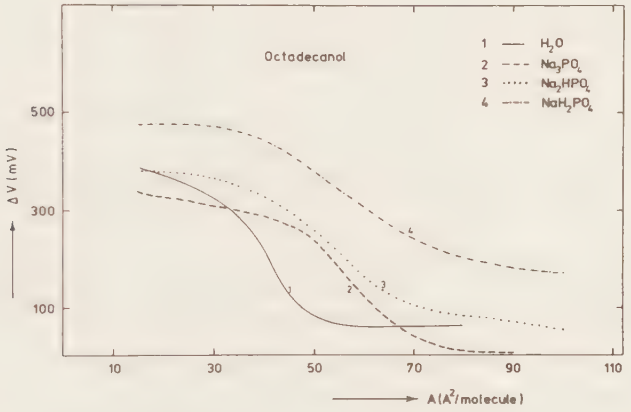


Fig. 51. The ΔV-A curves of octadecanol on distilled water and 0.1m solutions of various phosphates at 24.5 °C.

A similar effect is found by spreading TFO on the phosphate solutions as for OD. Fig. (52) shows the curves of TFO on water, sodium hydrogenphosphate and sodium dihydrogenphosphate. In the three curves the surface potential of the TFO monolayer increases smoothly, but at about 40 $Å^2$ molecular area a turn in the curve leads to the rapid increase of the ΔV values with decreasing area. This turning point indicates some changes in the structure of the monolayer and is also observed in the F - A curves of TFO (fig. 11). The order of increase in the surface potentials of the molecules of the monolayer is found to be:

$$H_2O < Na_2HPO_4 < NaH_2PO_4.$$

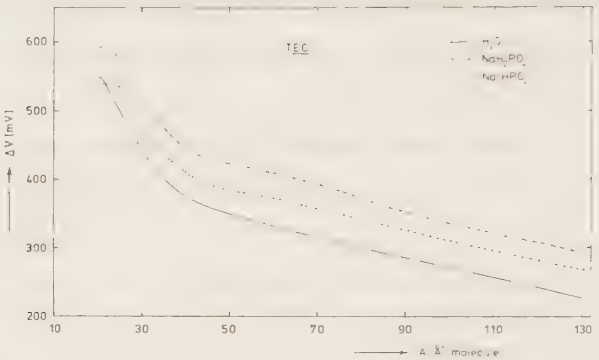


Fig. 52. The ΔV-A curves of TEO on distilled water, sodium monohydrogenphosphate, and sodium dihydrogenphosphate at 24.4 °C.

4.5.4 Surface potential of EO and pH of trough solutions

It is generally recognized that the behaviour of the nonionic surfactants is almost independent of the pH effects [54, 74, 83]. However, at the lower values of pH an enormous increase in the surface potentials of methyl-n-octadecylether and nonylphenol + 15 EO has been reported by Schulmann and Schick [54,74]. They changed the pH of the solution with a very low concentration of hydrochloric acid. Their results are reproduced in fig. (53). Two ranges of pH can be observed, one between 3 and 14, where the nonionic surfactants are insensitive to pH changes and the other range below pH = 3, with remarkable effects. At low pH values the surface potential increases, owing to possible oxonium ion formation[74]. On the other hand it is confirmed from fig. (53) that the surface potentials between 3 and 14 pH values remained unchanged. To seperate the pH effects,if they exist, from the electrolyte effects upon the derivatives of EO is very difficult. Maclay[83], however,

was able to distinguish the pH effect from the salt effect by measuring the cloud points of the adduct of t-octylphenol + n EO (Triton x-100), first without buffer solution and then with buffer solution of Na_2HPO_4 in 2% Triton solution. For each nonionic

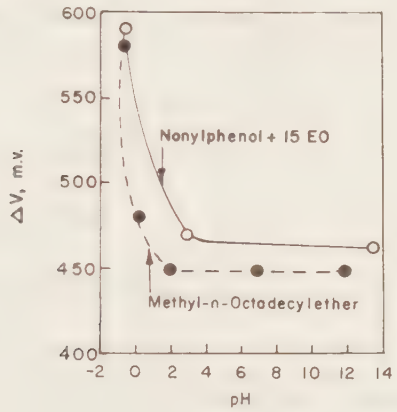


Fig. 53. Effect of pH on the surface potential of 2 10^{-4} mole/l nonylphenol + 15 solution [74], and the monolayer of methyl-n-octadecylether [54].

emulsifier there exists a temperature, generally called as "cloud point", at which the degree of hydration of the hydrophilic portion is just insufficient to solubilize the remaining hydrocarbon fragment, consequently, the emulsifier seperates from the solution[83].

Table XIII: Cloud points (C.P.) of Triton x-100 with and without buffer soultion of Na_2HPO_4.

HCl/Triton solution		contribution of buffer components to the cloud points (C.P.) of Triton x-100		
pH	C.P. (°C)	g. Na_2HPO_4/100g 2% Triton solution	pH	C.P. (°C)
1.4	64	0	6.73	64
3.0	64	0.49	8.87	61
5.2	64	0.97	8.98	58
7.2	64	1.45	8.92	55.5
		1.94	9.0	52.5
		2.65	9.0	48.0

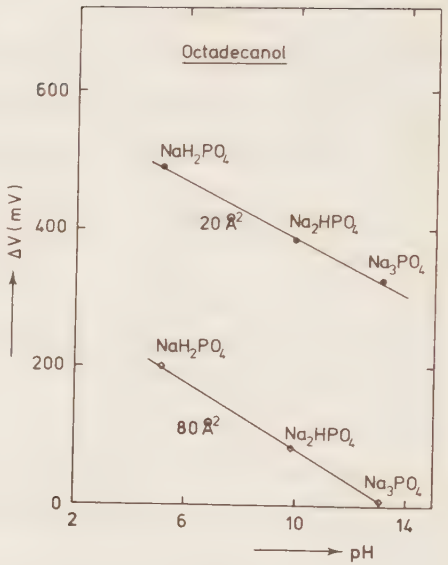


Fig. 54. Surface potential of the monolayer of octadecanol plotted against the pH of various phosphate solutions of 0.1m concentration at 24.5 °C.

Maclays results are reported in table VIII, from which it becomes evident that the decrease of the cloud points is dependent upon the concentration of a component (Na_2HPO_4)of the buffer solution, but independent of the pH variation.

On plotting the ΔV values of OD on Na_3PO_4, Na_2HPO_4 and NaH_2PO_4 against the pH values, straight lines are obtained for two representative areas of the expanded and the condensed states (fig. 54). Apparently the fig. (54) shows a pH effect, but on the basis of the above discussion it could only be regarded as an electrolyte effect. From the different results it can now be concluded that it is the salt which influences the properties of nonionic PFO monolayers and not the pH of the trough solution.

5. Experimental

5.1 Chemicals

To have a stable monolayer at the air-water interface, the spreading substance and the spreading solvents must be insoluble in water and highly purified. Any small amount of impurity in the trough solution may change the properties of the monolayers.

5.1.1 Spreading substances

The originally available substance p-iso octylphenol + 5.7 EO (PIOP-5.7) did not form stable monolayers, since the loss of the film material was too large because of its solubility in water. The solubility of PIOP-5.7 into water was found spectroscopically 0.121 g/L, which is quite high for monolayer purpose.

To avoid the problem of solubility new substances with longer hydrocarbon chains and shorter hydrophilic groups, i.e., $C_{18}H_{37}(OCH_2CH_2)_nOH$ (n=1,2,3), were obtained from BASF (Ludwigshafen) and $C_{18}H_{37}(OCH_2CH_2)_3OH$ was obtained from Henckel (Düsseldorf). The early results obtained from substances of both sources raised the doubts about the purity of the substances, since the results of both TEO (n=3) were not in agreement. The nonionic surfactants could exist in mixtures, as long as they were prepared by the addition of ethylene oxide to the molecules containing an active hydrogen. It was therefore necessary to purify the substances and seperate such possible mixtures of various homologues into individual members. The chromatography method has been used to seperate the individual members of PEO.

5.1.1.1 Thin layer chromatography (TLC)

For the purpose of identification of the substances thin layer chromatoplates (DC-Alufolien, Aluminiumoxide-F 254 type I, Merck, W. Germany), containing 0.2mm thick layer of aluminiumoxide serving as stationary phase, were used. As mobile phase a mixture of n-Hexan and Acetone (2:1) was chosen.+ A very small amount of each substance of both sources have been put from their 0.1m solutions in chloroform on the chromatoplate with a fine pipette. The chromatoplate was put in the tank containing mobile phase of n-Hexan: acetone (2:1) for the development. It took about one and half an hour that the mobile phase percolated fully along the plate, which was taken out and dried. To identify the spots on the plate the iodine quenched fluorescence method has been used, which may detect very small amounts and the overlapping spots as well. By exposing the developed plate to the iodine vapours, the brown spots became visible. It has been observed that the substance from BASF produced a number of spots ending in a tail on the plate, whereas the substance (TFO) from Henckel produced only one spot. By this experiment it could be proved that BASF substances existed in mixture and are needed to be purified, but the Henckel substance showed sufficient purity.

5.1.1.2 Preparative TLC

To separate the individual members of PFO from the mixture substances of BASF, preparative TLC has been used. In preparative TLC the sorption layer of alumina or silica gel is thicker (~1.5mm) than in TLC. The following steps have been taken to extract the series of ethylene oxide products.

+ The cooperation of Dr.W.Scoeler in TLC experiments is highly acknowledged.

a) Preparation of plates

A slurry of silica gel was prepared by mixing 1kg of silica gel (60 PF, Merck) into 2.2 litre of distilled water. Twenty glass plates (400 x 200mm) were cleaned and dried for spreading the slurry of silica gel on them. With the help of a divice consisting of a moving spreader and a stationary spreading board (fig. 55), silica gel slurry was spread uniformly on the

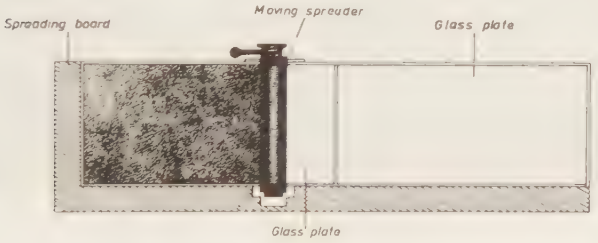


Fig. 55 The spreading board and spreader for coating the glass plates with silica gel layer.

glass plates. The thickness of the slurry was adjusted 1.5mm at the spreader. To activate the silica gel layers the plates were left at room temperature overnight.

b) Development of plates

One litre of n-Hexan:acetone (2:1) mixture as mobile phase was taken in the developing tank, which was then closed to ensure the saturated admosphere inside the tank. With a fine pipette the compounds to be separated were applied in a straight line three cm above the bottom of the plate. Ten plates at a time

in a carrier were placed vertically in the tank, containing mobile phase for the development of plates. The development took about two hours till the mobile solvent percolated the adsorbant to a few centimeter below the upper end of the plates.

c) Extraction of compounds

After drying the plates in an oven, a number of grooves appeared on the plates indicating different compounds (see fig. 56). The grooves were visible under an UV lamp. Each row or groove on the plate was scrapped off separately by a fine spatula and collected in a breaker. Acetone dissolved the separated organic compound and was removed from silica gel by glass filters. By means of rotavapor the solvent acetone was evaporated and the solid EO compounds were obtained.

d) Results and Rf

Quite a reasonable resolution was observed, which made it possible to seperate the required fractions. Fig. (56) shows the photograph of one of the plates developed by preparative TLC. Seven fractions can obviously be recognized, showing the compounds containing EO units from 1 to 7. The various compounds were tested and identified on a 0.2mm Al_2O_3 TLC plate using octadecanol and trioxyethylene-octadecanol (Henckel) as reference substances.

The Rf value is simply a convinient way of quoting the position of a compound on a plate as a decimal fraction, since it is defined as following,

$$Rf = \frac{\text{Distance moved from its origin by a compound}}{\text{Distance moved from its origin by a solvent front}}$$

The distance moved by the compound is normally measured from the centre of the spot or groove. On plotting the Rf values of

Fig. 56. Preperative thin layer chromatoplate developed in n-Hexan:Acetone mixture showing the seperated grooves of different compounds of polyoxyethylene-octadecanol.

the compounds found in the grooves of the plate shown in fig. (56) against the number of EO units, a linear relationship has been found in fig. (57). With the increasing number of EO units, the decrease in Rf is due to the stronger adsorption of higher members of PEO than the lower ones. The reproducibility of Rf values is quite good, i.e. ± 0,01. The Rf values of TEO (Henckel) and the newly extracted TEO are well in agreement (± 0.001).

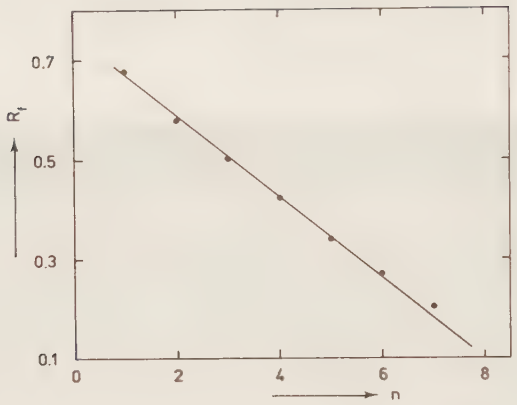


Fig. 57. The Rf values of PFO compounds extracted by preparative thin layer chromatography with silica gel adsorbant layer (~1.5 mm thickness).

5.1.2 Spreading solvent

It is to be desired that the solvent shall accomplish the dispersal of the spreading molecules at the air-water interface and then disappear completely from the scene. The volatility and water-solubility of the spreading solvent presents a more complicated problem. The solvents, which boil in the range of 40 - 80 °C are generally most suitable for experiments under ordinary conditions [49]. Chloroform (GR, Merck) has been taken as spreading solvent, which had the purity of 99.5 - 99.8 %. It boils at 61 °C and has a sufficient solvent power for PFO. Chloroform is least soluble in water and its evaporation after spreading the monolayer is fast enough.

5.1.3 Subphase

The purity of the subphase in the trough is of utmost importance. The trough water was always taken doubly distilled, first with potassium permagnate and alkali.* All the salts used in the trough solution were obtained from Merck (Darmstadt) and possessed above 99 % purity. Before using the salt solutions as subphase, they were filtered out.

5.2 Apparatus

The apparatus used for the measurements of surface pressure includes the Langmuir metallic trough and the Wilhelmy film balance. The surface potential was measured by a vibrating plate electrode on a circular teflon trough. Amplifiers and recorders were used to record the results automatically.

5.2.1 Trough

The most F-A data of PEO monolayers were obtained by using a Langmuir trough [84], whose inner dimensions were 30 x 20 x 1 cm. The said trough was made of stainless steel and sprayed with teflon (polytetrafluor ethylene). To inclose the film area two glass barriers (29 cm) and two teflon barriers (18.5 cm) were used. The float (18.5 x 18.5 cm) was made of polypropylene teflon combination [85] and was driven forward and backwards by an electric motor and gear. Two water sucking devices were fitted on the front and rear part of the trough. Some other accessories, such as a pH-electrode, thermometer and a Wilhelmy balance, were mounted on the trough as well. The lower part of the trough was made up double-walled in order to circulate the thermostated water. To avoid the air-contamination a cover made of transparent plexyglass has been put onto the trough.

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* The assistance of Miss G. Dahm is highly acknowledged, who provided the distilled water.

The trough was placed onto a cemented table. A photograph of the modified newly constructed trough* is shown in fig. (58), which reflects almost all the parts mentioned above. The circular teflon trough [86] used for the surface potential and partly for the surface pressure measurements was borrowed from the Max-Planck-Institut, Göttingen.

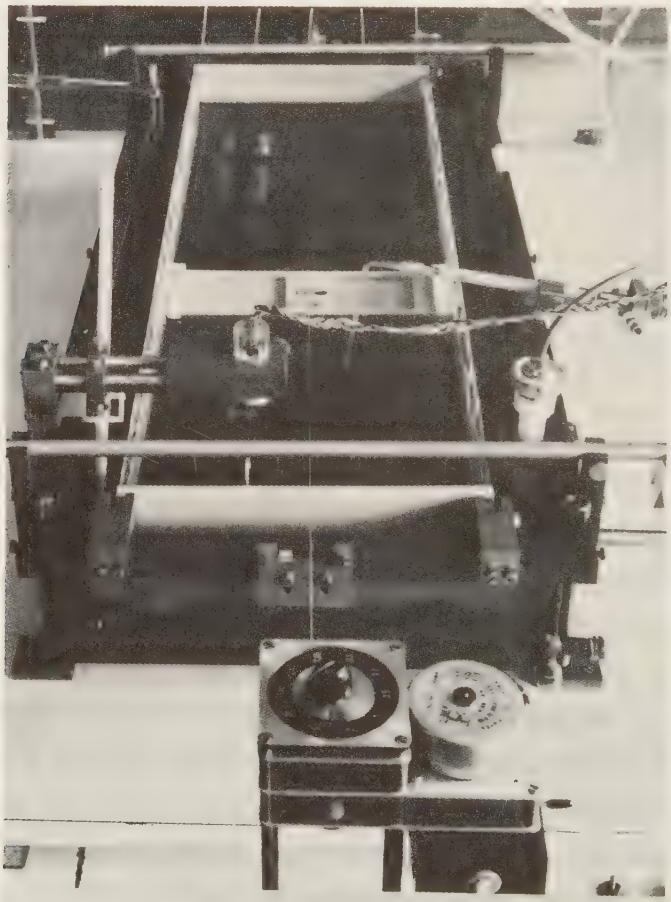

Fig. 58. The apparatus to measure the F-A diagrams of monolayers

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* Thanks are due to Mr. Graf, who built the trough.

5.2.2 Film balance

The surface pressure of a spread monolayer is the reduction of the interfacial tension of the clean surface of a liquid substrate. Two types of film balances are generally used for measuring the surface pressure: the Langmuir type (40) and the Wilhelmy type (87).

The Langmuir type is a horizontal float balance, which utilizes a direct differential measurement. A reference clean surface is seperated from the film covered area by a partition and it is the force acting on this partition, which is measured. However, the leakage problem of the film material is very serious as it is very difficult to keep the reference surface clean. A detailed description of a Langmuir balance is given by Gaines (49) in his book "Insoluble monolayers".

The Wilhelmy type, a vertical pull film balance, gives an absolute measurement method. Here the force observed is due to the surface tension on the plate partially immersed in the liquid with a monolayer on it. A clean reference surface during the experiment is not needed in this case, however, the water surface must be extremely clean before spreading of film material. The Wilhelmy balance (44) used for our experiments is shown in fig. (59). In this balance a blade of stainless steel, of 15 x 0.4 mm cross section, is used as reed spring, which is fixed at one end. The free end of the spring is provided with an iron core, which is a part of a transducer, and a hook for the Wilhelmy plate and the calibrating weight. The balance signals are transferred through the transducer to the amplifier or monofilmmeter, which signals further to the recorder (RF 511 compensation recorder, Metrawatt). The effective length of the spring is about

70mm and the deflection is 0.8mm for a weight of 310 mg, which corresponds to a surface pressure of 50 dynes/cm for a plate of 6.1 cm circumference. As Wilhelmy plate a 3 cm wide and 0.5 mm thick

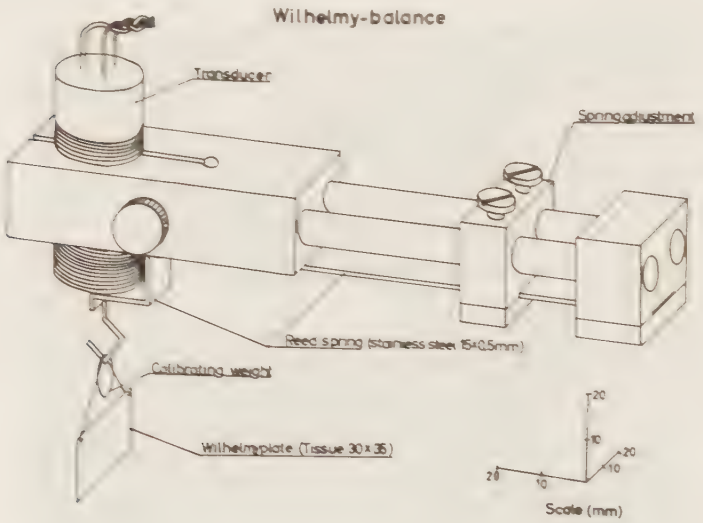


Fig. 49. The Wilhelmy balance for measuring the monolayer surface pressure.

piece of filter paper 'blueband, Schleicher and Schüll' has been used. The capillary rise in the paper assured a constant contact angle of 0°. Den Englesen [88] reported that the error due to the possible adsorption of surface active material is negligible. The precision of the balance was upto 0.1 dynes/cm.

5.2.3 Surface potential electrodes

The surface potential of monolayers can be measured by two ways, by an ionising-electrode and the vibrating-plate method.

Bellamy et el.[89] showed that the results of both methods agree within precision of the measurements.

The ionizing-electrode method involves ionization of the gas above the film, so that it becomes conducting. The ionization of the air is usually produced by an air-electrode on which a radioactive material is mounted. The α -particle sources, like polonium (^{210}Po) or americium (^{241}Am) are usually preferable, as such sources produce an intense ionization.

The vibrating-plate electrode method is based on the principle that if two surfaces, having different electrostatic potentials, are moved with respect to one another, a current will flow in an external circuit. With the vibration of the electrode about 2 - 3mm above the water surface, the capacity of the air-gap changes. This change leads to the current flow in the external circuit. The magnitude of the current is proportional to the potential difference across the gap. A circuit diagram of the vibrating plate [44] has been reproduced in fig. (60), which shows the important parts of apparatus for measuring the surface potential of monolayers. The glass rod fixed at one end, which is vibrating at its resonance frequency, bears at the free end a 0.2 mm thick platinum disk (VP). The small magnet dipped in a coil faces to an iron plate fixed with the glass rod. The magnet receives the signal, which is induced in the coil and amplified to a constant amplitude. The vibrating-plate electrode and a vibracondensator (high resistance amplifier and null detector) was borrowed from the May-Planck-Institut, Göttingen. A calomal electrode was used as the trough electrode.

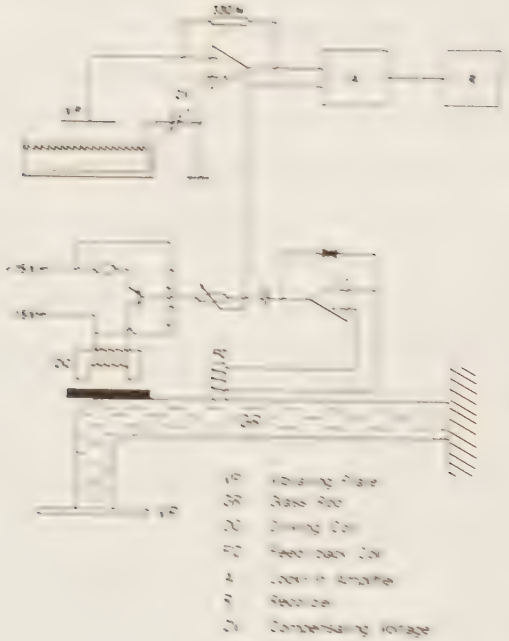


Fig. 3. Circuit diagram of a vibrating-plate-type apparatus for measuring the surface potential.

5.3 Methodical

Before taking the reading the apparatus was set at constant temperature. pH and temperature of the trough solution were noted for every run. The water surface was cleaned before and after each experiment with a sucking pump. As a control the float was run on the water surface without any monolayer on it. If the surface without monolayer is clean enough, no pressure can be detected, which gives the zero line for the next reading with

monolayer. This proves to be a contamination test. If due to any contamination the pressure was raised to more than zero, 0.5 or 1 dyne/cm, the water surface was cleaned once again before spreading the monolayer.

The 10^{-3}m solutions of all the substances studied were prepared in chloroform (GR, Merck), which was used as a spreading solvent. With the help of a microsyringe (agla, Burroughs Wellcome and Co) a known volume of a substance (~ 0.05ml of 10^{-3}m soln. ~1% error) is spread out dropwise. Usually the monolayer was left for three minutes, so that the chloroform could evaporate completely. The monolayer was then compressed by pulling the float with an electric motor and a gear at a speed of about 5 cm per minute. During the compression of the monolayer the F-A diagram was recorded with a compensation recorder (RE 511, Servoger). After completing one reading the monolayer was removed by a sucking pump and the water surface was cleaned for the next reading.

5.3.1 Calibration of Wilhelmy balance

The total area of the rectangular metalic trough (RMT) is 600 cm^2, but the area available to spread the monolayer was 370 ± 1 cm^2. The number of the spread molecules could be calculated from the known volume of the spreading solution. Hence the area per molecule can be calculated.

The circular teflon trough has a maximum area of 360 cm^2 and the area available to the monolayer (310 cm^2) could be adjusted through the amplifier (monofilmmeter). The total area (361,5 cm^2) of the circular trough was calculated also by measuring the radius of the trough, which is quite in agreement with the area read on the monofilmmter (~ 0.5 % error).

In the Wilhelmy balance a thin plate of filter paper (3 x 4 x 0.05 cm) has been used. The forces acting on the filter paper, suspended in subphase liquid, then consist of the gravitational and surface tension effects, downward, partially offset by the buoyant effect due to the weight of the liquid displaced[49]. The usual procedure for the use of a Wilhelmy balance involves maintaining the plate completely wetted by the liquid (filter paper ensures such requirement) and measuring the net downward force F_g for the plate, when the surface tension is altered by means of a monolayer. The changes in the surface tension, i.e. film pressure, gives the deflections to the balance. For the calibration of the balance the following equation is applicable[49],

$$F = -\Delta\gamma = -\frac{\Delta F_g}{2(t+w)} \quad \ldots\ldots \qquad (24)$$

where t and w are the thickness and width of the plate, F is surface pressure and ΔF_g is the net downward force. However, thickness is negligible, the above equation reduces to

$$F = -\frac{\Delta F_g}{2w} \quad \ldots\ldots\ldots\ldots\ldots\ldots \qquad (25)$$

A series of known weights are used to calibrate the film balance. Fig. (61) shows the calibration curve of the film balance mounted on the rectangular trough. For example, a weight(W) = 306 mg gives a pressure F = 50 dynes/cm for a three cm wide filter paper plate, which shows a deflection or signal(X) = 14.75 cm on the recording paper. For almost every new series of measurement the calibration of the balance was repeated.

The surface pressure by the film balance fitted on the circular trough, whose paper's width was 1.5 cm, could be read from the monofilmmeter. The calibration curves of this balance for two amplifications are shown in fig. (62), where, for example,

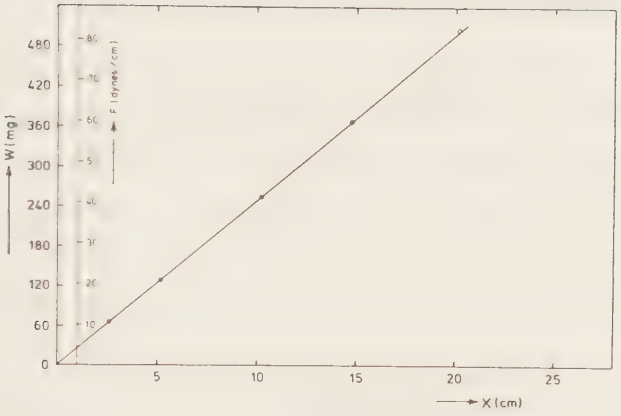


Fig. 61. The calibration curve of film balance fitted on rectangular trough with three cm wide Wilhelmy plate (filter paper).

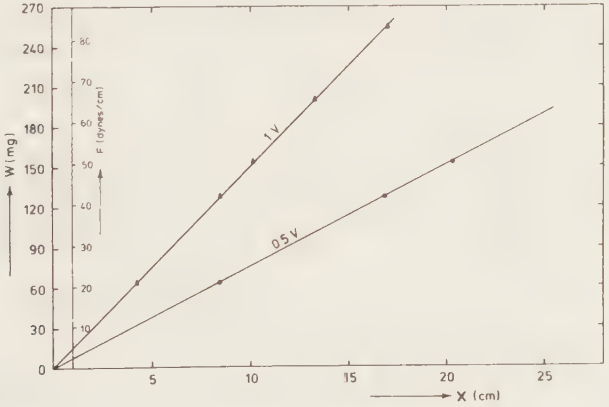


Fig. 62. The calibration curves of film balance mounted on circular trough with 1.5 cm wide Wilhelmy plate (filter paper).

a weight of 153 mg gives a pressure of 50 dynes/cm and shows the deflection(X)=10 cm and 20 cm for 1V and 0.5V amplifications respective

5.3.2 Calibration with stearic acid

The stearic acid is generally considered a standard substance for the calibration of the apparatus. Fig (63) shows the calibration F-A curve of stearic acid on the rectangular metallic trough. The extrapolated area of the solid part and the L_c -S transition pressure are well in agreement with the results of various workers given in table XIV. The extrapolated liquid-expanded area (24.5 $Å^2$) agree also with the literature values i.e. 24.3 [49], although there is no sharp kink at this area.

Table XIV. The extrapolated zero pressure area and L_c-S transition pressure of the stearic acid monolayer at the closest-packed solid state.

extrapol. solid area ($Å^2$)	L_c-S trans. pressure (dynes/cm.)	temperature (^oC)	subphase	reference
20.4	23.8	24	H_2O	this work (RMT)
20.6	16.0	20	H_2O	Casilla [90] et.el.
20.2	24.0	25	10^{-4}N H_2SO_4	Gaines [49]
19.3	23.2	25	H_2O	Harkins [91]
20.3	23.4	25	10^{-3} m $NaHCO_3$	Harkins [43]
20.4	24.3	25	pH = 3 H_2SO_4	Langmuir [92]
20.5	24.0	25	H_2O	Walkers & [93]
21.0	23.5	25	0.1 m HCl	Dreher & Sears [94]

The main discrepancy appeared with the circular trough. The extrapolated area per molecule of the stearic acid, for example, was found almost the same (~1% error), but the pressure of the

monolayers did not correspond to the values obtained from rectangular trough and to the literature. For instance, the monolayer

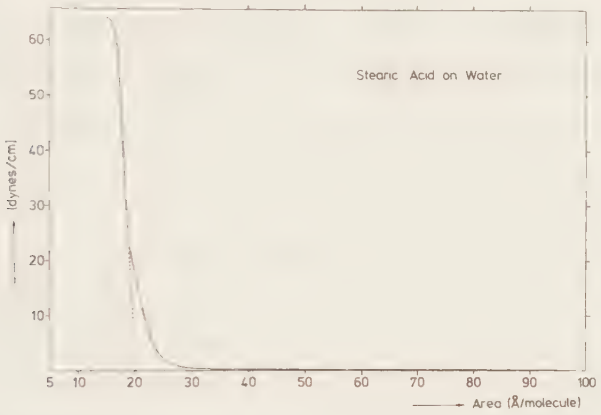


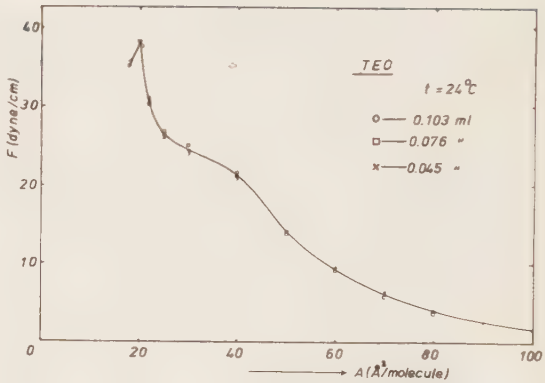
Fig. 63. The calibration curve of stearic acid at 24°C.

of TEO at some constant area, say 30 $Å^2$, gives a pressure of 24 dynes/cm with the rectangular trough, but 27.3 dynes/cm with the circular trough. There could be a number of reasons for this discrepancy, but major causes seem to be the different width of both filter papers used in both balances, the possible leakage of the film material and the different speeds of compression in both troughs etc. However, most of the results data presented in this work are produced by the F-A isotherms measured by the rectangular trough.

5.3.3 Reproducibility and Hysteresis

All experiments were performed 3-5 times. The results presented in this work are taken as average values. The experimental errors are reported with ($\pm$) error limit in the text. An example of mean value result is shown in fig.64. Similarly the reported surface potential results are also the mean values of 2-4 measurements.

Fig.64. The F-A diagram of TEO monolayer on water by RMT (mean value of three different measurements).



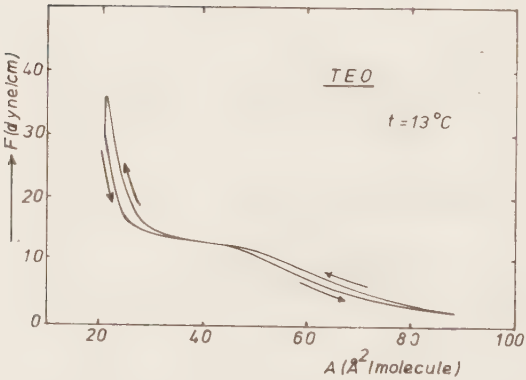
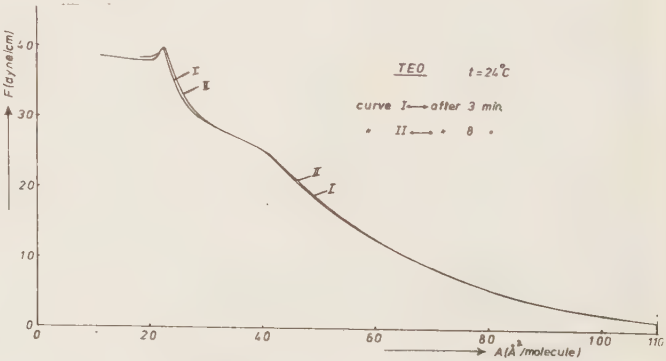


Fig. 65. The hysteresis of the F-A curve of TEO monolayer on water by RMT.

Fig. 66. Repetition of the F-A curves of TEO monolayer on NaSCN (0.1m) by CTT.



Further some experiments of hysteresis are also performed as shown in fig. 65. In hysteresis the monolayer is first compressed towards smaller area and then with same speed relaxed to its original area. Another sort of control is represented by fig. 66 , which shows that once the compressed monolayer of TEO is relaxed, the same monolayer is compressed again under same conditions.

6. Summary

The present work was aimed to investigate, whether and how the changed structure of water, either by temperature or by salt addition, affects the monolayer of polyoxyethylene-octadecanol (PEO). To avoid the electrostatic interactions nonionic surfactants of polyoxyethylene adducts were chosen to study, which are susceptible to hydration through hydrogen-bond formation. All the spreading substances have been first purified and seperated into individual members of PEO by preparative thin layer chromatography. The monolayers of PEO have been measured as F-A diagrams on Langmuir trough by Wilhelmy balance, and as ΔV-A curves with vibrating plate method.

The expansion of F-A isotherms of the PEO monolayers appears to be due to the increasing intermolecular interaction between the underlying water molecules and the hydrophilic part of the film molecules, when the number of EO units increases. The increasing interaction between EO and water molecules through hydrogen-bond formation may act as 'expansive force' against the 'cohesive forces' of the hydrophobic chains, hence the monolayers expand towards higher pressure and larger area with increasing hydrophilicity of the film molecules. The calculated energy of dehydration ($E_d = \int F.dA$) from the F-A curves of PEO increases with increasing number of EO units. Since the elavation of temperature breaks the associated structure of water and then the stronger interaction between EO and water overcomes the cohesive forces of aliphatic chains, the monolayers of PEO expand and the reverse happens by a decrease in temperature. By an increase of 10 ^{o}C the F-A curve of DEO was quantitatively similar to that of TEO and similarly a decrease of 10 ^{o}C made the TEO curve resemble to DEO.

The surface potential of the PEO monolayers increased, as the polarity of PEO became larger with higher number of EO units. The increasing of the surface potential with increasing EO units may be due to the orientation of more water molecules as well as the increasing dipole orientation of the film molecules themselves.

The intermolecular interactions between hydrophilic groups and subphase molecules become much larger when the salt is added to water, the monolayers of PEO expand showing higher pressure and larger areas.The intermolecular interaction and consequently the expansion of the monolayers is dependent upon the nature of the ions. The effectiveness of the anions is found almost in the Hofmeister series,i.e., $Na_2SO_4 < NaCl < NaNO_3 < NaClO_4$. The anions classified as structure-breaker like ClO_4^- showed larger interactions than the structure-maker,like SO_4^{--}. The energy of dehydration for OD and MEO on various salt solutions is found in line with the'structure-temperature' ($T_{str.}$) of various salts.

The expansion of PEO monolayers with increasing concentration of $NaClO_4$ is a direct consequence of the weakening of the water structure by presence of the latter. The free OH groups in water increase with increasing concentration of $NaClO_4$, which in turn make H-bonds with EO of the film molecules. The stronger interaction due to higher concentration of $NaClO_4$ caused the expansion of PEO monolayers,and the expansion corresponded to $T_{str.}$ of $NaClO_4$ at various concentration.

The surface potentials of PEO monolayers varied almost according to the Hofmeister series of anions.This may further cast some light upon the orientation of water molecules around the hydrophilic groups of the film molecules. With the help of the measurements on phosphate solutionns of different pH values and their

comparison with the other literature results (sect. 4.5), it has been shown that pH has no effect on the PFO monolayers,but only the salts in the subphase. The effects of soium (mono-,di-,and tribasic) phosphate are found in the following order of expansion of PFO monolayers,

$$NaH_2PO_4 < Na_2HPO_4 < Na_3PO_4 \quad .$$

On the basis of the results presented in this thesis it can now be concluded that the interaction between hydrophilic groups of film molecules and water by hydrogen bonds is a dominating factor in determining the properties of PFO monolayers. The structure of water influences the properties of PFO monolayers, when the former changes either by temperature or salt addition.The effects of various anions on the F-A isotherms of PFO,as on the water spectra also, are parallel to the Hofmeister series of anions. The presented results lead us to believe that the anions change the content of free OH groups in water, which in turn form H-bonds with ether oxygens of PFO molecules. Because of the stronger interaction between hydrophilic groups of the film molecules and the subphase it may be suggested that the F-A isotherms cannot be considered only a two dimensional phenomena.

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